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SYMPOSIUM ON

RARE METALS

HELD ON 1st, 2nd, 3rd DECEMBER, 1957

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CONTENTS

Page

India's resources in Rare Metals
by D. N. Wadia 1

Resources of Rare Metals in Burma
by Kyaw Nyun 8

Review of Beneficiation Techniques pertaining to Uranium Bearing Ores
by G. P. Mathur and P.I.A. Narayanan 12

Some aspects of the Dressing of low grade Uranium Ores and Beach Sands in India
by R. Krishnaswamy 21

The Extraction and Recovery of Uranium from Australian Ores
by T. R. Scott 27

Problems in the Leaching and Extraction of Indian low grade Uraniferous Ores
by J. Shankar and B. H. Krishna 40

The recovery of Uranium from Acid Leach Liquors by Anion Exchange
by T. V. Arden 48

Treatment of Monazite Sands with special reference to Indian Practice
by H. N. Sethna and S. Fareeduddin 68

Brazilian Practice for Monazite Treatment
by P. Krumholz 78

Applications of Rare Earth Metals in Metallurgy
by B. R. Nijhawan 83

The present status of Zirconium Metallurgy
by Brahm Prakash and C. V. Sundaram 95

The present status of Beryllium Metallurgy
by T. Banerjee and P. B. Chakravarti 114

Recent developments in Beryllium Metallurgy
by C. W. Schwenzfeier jr. 131

Present status of production of Metallic Uranium and Thorium
by S. K. Kantan and G. S. Tendolkar 150

Problems in treatment of Irradiated Fuel Elements and Breeder Blankets
by Rajindra Manocha 163

Recent developments in the Pyrometallurgical Treatment of Irradiated Fuel Elements and Breeder Blankets in U.S.A.
by Stephen Lawroski 176

Physical Metallurgy of Uranium
by K. Tangri and R. Somasundaram 194

British practice in Uranium Metal Fuel Element Manufacture
by L. M. Wyatt 247

Extrusion of Uranium, Zirconium and Co-Extrusion of U-Zr by the Sejournet Method
by J. A. Stohr 280

Recent Developments in the Physical Metallurgy of Plutonium
by D. M. Poole and M. B. Waldron 293

Physical Metallurgy of Thorium
by M. K. Madhekar and M. K. Asundi 311

Technology and Applications of Rare Metal Oxides and Carbides
by V. K. Moorthy 331

Special problems in the sintering of Beryllium Oxide
by R. Caillat 342

Powder Metallurgy in Nucleur Engineering
by Henry H. Hausner 351

Fundamental considerations in Alloying Behaviour of Heavier Metals
by J. Friedel 387

Preparation of Rare Earth Metals
by F. Trombe 402

Contributors to the Proceedings 445

SYMPOSIUM ON RARE METALS

The Symposium on **'Rare Metals'**, jointly sponsored by the Indian Institute of Metals, UNESCO and the Department of Atomic Energy, Government of India, was held in Bombay from 1st to 3rd December, 1957. As the principal aim was to focus attention on recent developments in reactor metallurgy, the scope of the symposium was confined to uranium, thorium, plutonium, beryllium, zirconium and the rare earth metals.

The symposium was inaugurated by Dr. H. J. Bhabha, Chairman of the Atomic Energy Commission, and was distinguished by the presence of several foreign delegates from Australia, Burma, France, U.K. and the U.S.S.R. and leading metallurgists from India. The participation of the foreign delegates was rendered possible largely due to aid given by UNESCO. Twenty-six papers—thirteen from India and thirteen from abroad, were presented and discussed at the Symposium in five sessions. This compilation is a record of the proceedings.

In presenting this volume, the organisers believe that it will offer a comprehensive picture of the diverse problems associated with rare metal technology. Rapid progress is being made in gaining an understanding of the complex behaviour of reactor metals, specially uranium and plutonium. Much, however, remains to be done and the symposium has spotlighted attention on outstanding problems such as the origin and prevention of radiation damage, production of ductile beryllium, and the highly complex metallurgy of plutonium.

Opening Session

In opening the proceedings, Professor G. K. Ogale, Vice-President of the Indian Institute of Metals, who was in the chair, welcomed Dr. Bhabha and the delegates to the Symposium. He expressed his gratification at finding so many distinguished delegates participating in the deliberations.

Inaugurating the Symposium, Dr. Bhabha said that atomic energy had opened a vast field of activities where there was great scope for research. He specially referred to the role which metallurgy has to play in the development of materials required for nuclear energy programmes. A study of the economics of power generation in India had revealed that atomic power would be economical in many parts of the country. Explaining the factors which were responsible for making atomic power economically competitive with power derived from coals, he said that coal fields in India were concentrated mainly in the Bengal-Bihar

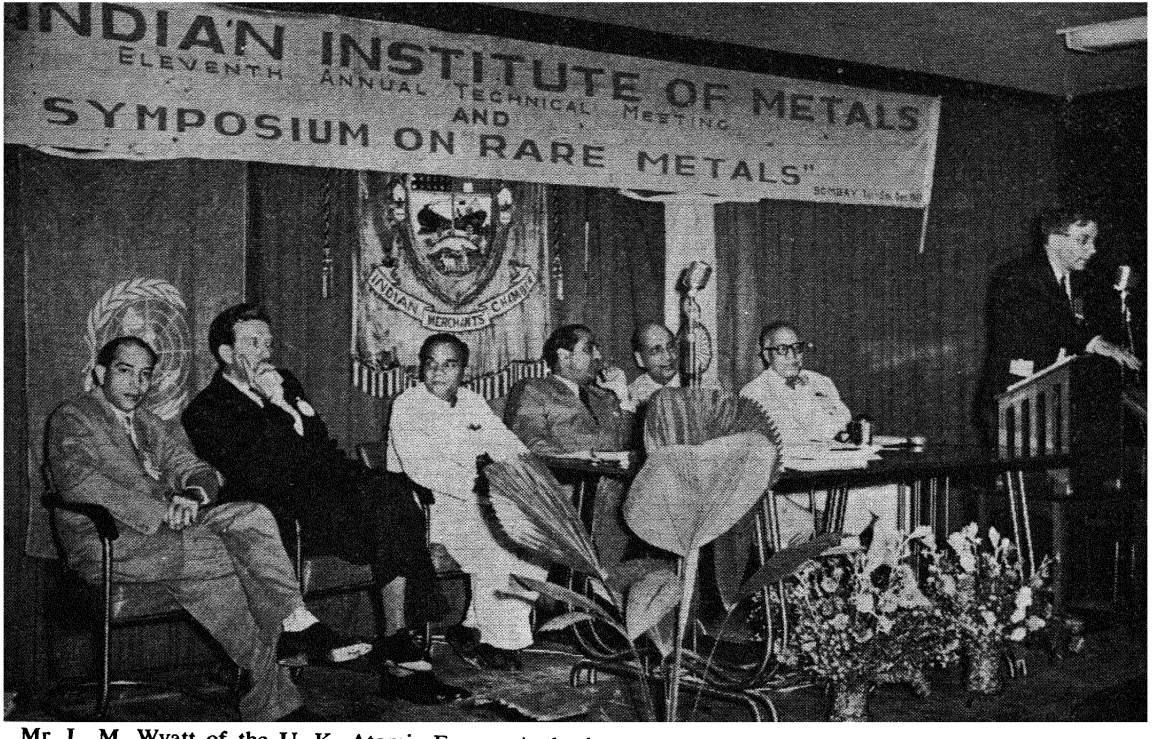
region so that coal had to be hauled to distant industrial areas in other parts of the country. This raised the cost of coal. If the cost of thermal power in these regions was not unduly high, it was because the transport of coal by railways was subsidised. In the interests of the economy of the country as a whole, it was, therefore, better to base power generation at places distant from the coal fields on something other than coal. If that could be done, it would enable the railways to carry other materials instead of the un-remunerative transport of coal. Another factor that would make atomic power economical in India was the shortage of power at present in industrial areas, which resulted from underplanning of power needs there and led to high load factor. This was a condition in which atomic power stations could be operated economically, retaining the present thermal stations for carrying peak loads.

Dr. Bhabha then summarised the various factors which govern the choice of structural, fissile, moderator and control materials in the construction of reactors. In conclusion, he said, that steps were being taken to produce all the materials required in the country. He referred to the treatment plant for beach sands in Kerala, and the thorium extraction plant at Trombay which were in operation, and the plants for uranium metal production and its fabrication into fuel elements which are under construction. A heavy water plant was being set up in Nangal where the cost of production would be very low—lower than in America, which was the cheapest in the world.

After the inauguration, Mr. William J. Ellis, Director of UNESCO, South Asia Science Co-operation Office, New Delhi, on behalf of the Director-General of Unesco and himself, extended a welcome to all the delegates gathered for the Symposium and explained briefly the role of UNESCO in fostering international co-operation in the field of science and technology. He was grateful to the foreign delegates for having accepted the invitation of UNESCO to participate in the symposium.

Responding to the welcome, the foreign delegates present, Dr. T. R. Scott of the C.S.I.R.O. (Australia), Dr. R. Caillat of the Commissariat A L'Energie Atomique, (France), Mr. L. M. Wyatt of the U.K. Atomic Energy Authority, and Professor E. I. Mojzukhin of the USSR, conveyed the greetings of their respective organisations for the success of the symposium.

In bringing the inaugural session to a close, Dr. D. P. Antia, Honorary Secretary of the Indian Institute of Metals thanked UNESCO, the Department of Atomic Energy, and the Bombay Chapter of the Institute for their co-operation in organising the symposium and expressed his thanks to the contributors of papers to the Symposium.



Mr. L. M. Wyatt of the U. K. Atomic Energy Authority responding to the welcome to foreign delegates to the Symposium. Sitting on the dais from left to right are—Dr. D. P. Antia **(Vice President of the Indian Institute of Metals),** Mr. William J. Ellis **(Director, UNESCO),** Prof. G. K. Ogale **(Vice President of the Institute),** Dr. H. J. Bhabha **(Chairman of the Atomic Energy Commission),** Mr. K. C. Mahindra **(Industrialist)** and Dr. S. R. Malhotra **(President of Bombay Chapter of the Institute for 1957).**

INDIA'S RESOURCES IN RARE METALS

*By D. N. Wadia**

In this paper the occurrence, origin and composition of some of the minerals containing rare-earth metals, are presented. A brief description of some of the atomic minerals, more particularly those of uranium and thorium, is also given. The reserves of monazite for which India is famous, are estimated at over two million tons.

The symposium includes papers on the rare earth metals and other rare metals like U, Th, Zr, Be, etc. The present paper briefly deals with India's resources in these metals.

Rare Earth Elements

The name "Rare Earth" was given to the oxides of a group of 15 metallic elements of very similar chemical properties but of restricted occurrence in nature. Some of these are in fact more common than the familiar metals, molybdenum, tungsten, tin, gold or even lead and zinc.

These rare-earth elements are classified into two groups : (1) The cerium group and (2) the yttrium group. Despite similiarities in chemical and physical characteristics and properties, minor differences do exist among them. Today they have all been separated in a pure state and their individual characteristics studied.

The cerium group of rare earths is of much wider occurrence in a large number of natural mineral combinations. It is also more intensively studied and is more widely employed in industrial and technological applications than the yttrium group, the utilization of which in the world's industry and commerce is yet inconsiderable. A noteworthy peculiarity of the rare earths is their tendency to occur in groups, or associations of several distinct units in mineral combinations, because of their similarity of chemical properties. Commercial and industrial uses of these minerals are based on this property of group associations, several of rare earths behaving alike. Few single oxides and sulphides of rare earth metals occur as mineral species and no native rare earth metal is known.

Geology : The rare earth minerals do not generally occur as primary constituents of rocks in any concentrated veins or lodes; they are most commonly found in pegmatitic segregation or as subordinate accessory minerals in granite or other igneous and volcanic rocks. Commercial sources of these metals, therefore, are coastal beach-sands or river placer deposits, derived from the disintegration of large rock-bodies,

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accumulated in course of geological ages, rather than mines working underground pegmatitic veins or bedded deposits. The only known examples of bedded, or concentrated vein deposits of rare earth metals in the world, of any considerable magnitude, are pegmatitic masses of monazite of India and the large rich vein deposits of bastnaesite, a fluocarbonate of cerium metal group, of California. Littoral and alluvial deposits of monazite are of more widespread distribution and form the world's main sources of rare earth metals which are coming increasingly in demand in industry and technology. Uses of these minerals and metals have been developed at a fast rate in production of glass and ceramics, pyrophoric alloys of the mischmetall type, steel and light metal alloys, electronic, photographic and cinematographic applications.

India's Resources in Rare Earth Metals

Monazite : The main ores of Indian occurrence from which rare earth metals can be extracted are monazite, allanite, xenotime, samarskite and pyrochlore. Of these, the commercially most important is monazite, which is the only one that is at present put to any commercial use for the extraction of cerium and allied salts and the oxides of thorium and uranium. India's resources in a wide group of rare earth metals are symbolised in its unique alluvial and placer monazite deposits. The monazite is a portmantau mineral, packed with an extraordinary number of rare earth compounds. It is truly a wonder mineral, being a compound of some 15 to 19 rare metals. It is a monoclinic ortho-phosphate of cerium and yttrium groups, besides carrying varying amounts of thorium and uranium as accessories, the exact molecular constitution of which is not yet well-established.

The full chemical composition of a representative sample of Monazite from Travancore is given below in the following table, taken from S. J. Johnstone.[1] It is derived from the beach sands, where over a million tons of this mineral is found as an ingredient of the well-known ilmenite sands.

Chemical composition of Travancore Monazite

	Per cen.
Thoria, ThO_2	8.1
Ceria, Ce_2O_3	30.6
Lanthanum Oxide, La_2O_3	15.7
Praseodymium Oxide, Pr_2O_3	2.9
Neodymium Oxide, Nd_2O_3	10.5
Europium, gadolinium and terbium oxides.	0.7
Yttrium Oxide, Yt_2O_3	0.4
Dysyprosium, holmium, erbium, ytterbium and lutecium oxides	0.1
Alumina, Al_2O_3	
Lime, CaO	1.0
Iron Oxide, Fe_2O_3	
Uranium Oxide, U_3O_8	0.3
Phosphoric acid, P_2O_5	26.2
Loss on ignition, H_2O	—

Other varieties of monazite from different parts of the east and west coasts of India show considerable variations in their cerium content from 20 to 31 per cent, Yttrium content from 1 to 1.5 per cent and of remaining rare earth oxides from 21 to 30 per cent.

An interesting variant of monazite known as green monazite, and lately described[2] as a new mineral under the name of 'cheralite', contains much less proportion of the rare earth oxides and much larger amounts 29 to 33 per cent. of thorium oxide and 4 to 6 per cent of uranium oxide. Although the main habitat of monazite sands are the east and west coasts of India, within the last few months, even larger deposits of detrital monazite have been discovered, capping the tops of certain plateaus in the Bihar State. Beside these secondary detrital deposits, monazite occurs as a primary mineral also in a number of pegmatites, specially of charnockite and allied granitic rocks, in various inland parts of the country, though they are not yet commercial sources of the mineral. The Indian Atomic Energy Department has undertaken a quantitative survey of the total reserves of monazite on an all-India basis; it is not complete yet, but the provisional estimates place the total reserves of this mineral of great potential value at considerably over two million tons, yielding well over 400,000 tons of combined rare earth oxides.

The remaining rare earth minerals are briefly dealt with :—

Allanite (Silicate of cerium, yttrium and iron) containing 2 to 34 per cent cerium earths, occurs in pegmatites in the crystalline rocks in various parts of India, at places in bulk aggegates of some cwts., as for example in Nellore and in parts of Orissa and Bihar.

Samarskite is a tantalo-columbate of the rare earths, carrying varying amounts of iron and uranium, cerium group oxides, 2 to 5 per cent, and yttrium group oxides, 5 to 21 per cent. Samarskite is a fairly widespread mineral in the micapegmatites occurring in Archaean complex of Rajputana, Madras and Bihar.

Fergusonite, with a more or less similar composition, has been observed along with samarskite in some of these pegmatites.

Xenotime (yttrium phosphate) contains 54 to 64 per cent yttrium group oxides. This mineral has not been found in any appreciable quantity in India; isolated specimens in well-formed crystals have been observed at different places.

Gadolinite (silicate of yttrium, iron and beryllium) contains 30 to 45 per cent of yttrium group oxides; it is found in tourmaline pegmatites in Rajputana. These minerals are, however, yet in the nature of museum specimens and are not put to any economic use.

Other rare metals of India

The above described cerium and yttrium groups of metals, conventionally called rare, by no means exhaust the list of what may more appropriately be designated as the Rare Metals of India. Amongst these are to be included the atomic metals—uranium, thorium, beryllium, lithium and zirconium; the less common metals of strategic value in the alloy industry such as molybdenum, titanium, tantalum, columbium, tungsten, vanadium; and metals used in some highly specialised industries—gallium, germanium, hafnium and tellurium. A brief account of these should, therefore, be added, as any sketch of India's resources in rare metals would not be complete without inclusion of the latter.

This subject has been dealt with by me in some detail in my paper[3] on the 'Strategic Metals of India'. Here only a few brief notes are given.

Atomic Metals

Thorium : The most important of these are uranium and thorium. India's resources in thorium, a possible 'fertile' metal of the near future, are on a large scale—the present estimates put the figure at about 250,000 tons. The source of this metal, as already stated in the earlier section of the paper, is the mineral monazite.

Uranium : Uranium occurs as disseminations and impregnations in Archean crystalline schists and pre-Cambrian metamorphosed slates and phyllites of Bihar and Southern Rajputana. It also occurs in pegmatites, but a more reliable source of uranium is the deposits of monazite beach and alluvial sands, as mentioned in the above paragraphs. Reserves of uranium in India available according to investigations carried out by the Department of Atomic Energy, are calculated at about 15 to 20 thousand tons. Further geological and geophysical surveys with air-borne radio-metric instruments are likely to reveal more of commercially workable uranium ores from other parts of India.

Beryllium : This rare strategic metal, of use in a number of valuable metallurgical alloys, beside its use in atomic energy, occurs as the mineral beryl in mica pegmatites in Rajputana, Bihar and Madras. The reserves of beryl (BeO 10 to 14 per cent) in India are considerable and will be able to meet all indigenous demands for atomic as well as metallurgical uses.

Lithium : This light metal has sprung into strategic prominence in experiments on the production of atomic energy through thermo-nuclear fusion of light elements. It is found in the minerals lepidolite 2.5 to 5 per cent Li_2O and spodumene (4 to 5 per cent Li_2O). The former mineral is fairly widespread in the mica belt of Bihar, the reserves of which are ample for future requirements.

Zirconium : India possesses large resources of this rare metal in the mineral zircon (ZrO_2-65 per cent) which forms about 6 per cent of the well-known ilmenite beach sands of the Indian coasts. Zirconium possesses some valuable properties, resistance to heat and corrosion, and has lately attained preminence as a structural and cladding material in atomic reactors. Cyrtolite is a radioactive variety, containing a small percentage of U_3O_8. An exportable surplus of zircon exists in India.

Alloy Rare Metals

Molybdenum : Molybdenite (MoS_2-Mo 60 per cent) is the principal mineral. It occurs in the Khasi hills, Hazaribagh district of Bihar and Godavari district of Andhra and also in the Madura district of Madras.

Titanium : The major source of this metal is ilmenite ($Fe\ TiO_3$) with 55 to 62 per cent TiO_2. It occurs as beach sands, "Black Sands" on the Malabar and Coromondal Coasts, as alluvial deposits in Bihar and also as vein deposits. The former is the most important source of the metal titanium. Estimated reserves are of a high order, calculated at over 200 million tons. Rutile (Ti 60 per cent) occurs in association with ilmenite sands in alluvial and placer deposits.

Columbium and Tantalum : The two minerals columbite and tintalite grade into each other by isomorphous replacement. The combined Nb-and Ta-oxides in them are generally high, ranging over 50 to 70 per cent. These minerals are found in large, coarse crystals at a number of localities, at some places, in parcels of a few cwts. bulk. They most frequently occur in association with beryl in pegmatites, traversing mica belts in Bihar, Rajputana and Madras.

Tungsten : The chief ore of this valuable strategic metal is wolfram (Wo_3 70 to 75 per cent). The mineral occurs very sparingly in Jodhpur and Nagpur districts in thin veins and stringers and also in a few aluvial deposits. Production has been fitful; barely a few hundred tons have so far been obtained from these localities.

Vanadium : This metal occurs in vanadiferous titanium-iron ores in igneous rocks in the Dalbhum and Mayurgunj districts of Bihar. V_2O_5 content is small, generally not exceeding 0.8 to 3 per cent, but the total volume of vanadiferous ore-bodies found in these districts is fairly extensive. Vanadium in traces is also observed in the ashes of some coals and lignites, both of Tertiary and Gondwana age.

The remaining rare metals occuring in India are of less importance.

Hafnium : It has been found as a fairly constant constituent of zircon along with zirconium (HfO_2 3.2 per cent). The metal is an absorbant of neutrons, like cadmium.

Rubidium : It has been found with lithium in lepidolite in insignificant quantities.

Gallium and Germanium : They are amongst the scarcest of metals, so far separated. Gallium has been observed in minute traces in some parts of India in ores of aluminium near Ranchi, some of the manganese-ores from Nagpur and gold-ore in Andhra. Germanium has been observed in traces in ashes of some coals from Assam and also from Singareni.

Tellurium : It occurs as telluride in combination with gold ores in Kolar and with copper-ores in Singhbhum and Assam.

The occurrences of the above-named rare metals are for the present of only scientific interest in India and there has so far been no commercial production of any of the last five metals.

Of the precious metals—gold, platinum, iridium, osmium, etc., with the exception of gold, the production of which has in the last few decades fluctuated from 600,000 fine ozs. to the current 200,000 fine ozs. per annum, mostly from the Kolar mines, Mysore, none of the other metals of this group occur in any appreciable quantity in India. Platinum, iridium, osmium have been observed in traces in the alluvial gold washings in Chhota Nagpur and Singhbhum and also in the Bauxite residues of Madhya Pradesh and Bombay.

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2. Bowie, S. H. U. and Horne, J.E.T., Mineral, May, 30, 96, (1953).
3. Wadia, D. N., Trans. Ind. Inst. Metals 10, (1957).

Discussions

Dr. L. M. Wyatt, (*Atomic Energy Authority, U.K.*) : I would like to ask how much of the ore mentioned in Dr. D. N. Wadia's paper is really economically workable? How much cheralite for example is there? Will it prove economic to work monazite deposits for their uranium content even if thorium is required as well?

Dr. T. R. Scott, (*Division of Industrial Chemistry, Commonwealth Scientific & Industrial Research Organisation, Australia*) : In Australia an ore of 0.3% U_3O_8 is regarded as quite satisfactory for production of uranium oxide concentrate. On the Blind River field in Canada and the Rand, South Africa, ores of 0.1% and less than 0.1% U_3O_8 respectively are being commercially exploited, the latter certainly as a by-product of gold mining. The fact that India can recover 0.3% U_3O_8 as a by-product of the processing of monazite places the country in a very happy position.

Dr. B. Prakash, (*Atomic Energy Establishment, Bombay*): I would endorse the statement of Dr. Scott regarding the grade of uranium ores. Uranium ores in India belong to three categories, namely, (a) low grade ores disseminated in Archaean and metamorphic rocks, (b) ores in pegmatitles such as pitchblende, and complex nibates, tantalates and titanates of uranium, and (c) deposits of monazite in beach sands which contain, on average 0.3 percent uranium. The low grade ores of the first category occur in Bihar and Rajasthan and their uranium content varies from 0.03 to 0.1 per cent.

The figure of 15 to 20 thousand tons mentioned by Dr. Wadia is based on the investigations carried out by the Atomic Energy Establishment, but intensive geophysical and geological surveys which are in progress are likely to reveal more of the commercially workable uranium ores. Cheralite is a rare mineral; it has no economic significance.

As far as the extraction of uranium from monazite is concerned, the extraction both of uranium and thorium from the beach sands will be covered in a subsequent paper which will be presented at the symposium by Mr. Sethna.

Few countries are as rich in high grade uranium ores as France, and perhaps our distinguished chairman Dr. Caillat would like to say a few words about the uranium deposits occurring in France and her colonies.

Dr. R. Caillat, (*Atomic Energy Commission, France*) : I believe uranium reserves in India are promising and use of minerals with low uranium content will be interesting. In France, at present, ores containing between 5 and 10% U_3O_8 are being worked. A considerable effort in prospecting for uranium ores in France is being made and fortunately there are many reserves in France. The Lebouchet factory is working on ores containing 5% U_3O_8 at present. Attempts are also made to utilise ores of low uranium content.

RESOURCES OF RARE METALS IN BURMA

By Kyaw Nyun *

A bief description of the localities wherein minerals of uranium and thorium are found in Burma, is given. Occurrence of minerals containing beryllium and rare earth metals has been reported but commercial production has not yet been started.

In the compilation of the following paper, attempt is made to include the latest findings by the Union of Burma Atomic Energy Centre. The standard books do not satisfactorily describe the occurrences of the minerals in question. But it must be noted that the Japanese invasion has left the country's prosperous mining and metallurgical industries in a most dilapidated condition. Subsequent insurgency has again contributed greatly towards the prevention of restoration of the mining industries. Hence, inspite of emphatic governmental effort on the development of mineral resources, no appreciable headway could be made on the scientific assessment of the country's natural wealth. So it may be noticed that there is no worth-while economic investigation mentioned in the paper. But once the presence of an economic mineral is known, it is hoped that, when appreciable peace is restored, economic prospecting would be just a matter of course.

Geological Background

Burma naturally falls into three great geomorphological divisions, namely :—

1. The Arakan Yoma on the west consisting of a great series of fold ranges of post-Cretaceous and Cretaceous age. Geographically, it is the Arakan-Naga region. It includes the serpentinised peridotites which carry chromite, native copper, chalcocite, chrysolite, steatite, magnesite and jadeite.

2. The Shan Plateau occupying the whole of east Burma extending into Tenasserim in the south and into Yunnan in the north. This division may be subdivided into :—

   (a) Shan-Yunan region composing of sedimentary rocks ranging in age from Cambrian to Cretaceous. The minerals are essentially sulphidic, such as argentiferous galena, sphalerite, chalcopyrite, pyrite and stibnite.

* Senior Research Officer in the Metallurgy and Geology Research Department, Union of Burma Allied Reesarch Institute, Rangoon.

(b) The Mogok comprises of gneisses and igneous intrusive rocks with crystalline limestone, notably the rubies, spinels and other precious stones.

(c) The Tenasserim Region composing quartzites and argillites of the Mergui Series with granite intrusion. The minerals are chiefly cassiterite and wolfram, with molybdenite, bismuthinite, chalcopyrite, pyrite, arsenopyrite, zinc-blende and stibnite occurring in small amounts.

3. The Central Belt of Burma. Composed mostly of Tertiary rocks. Petroleum, coal and amber are the characteristic minerals.

Uranium

The reference on the occurrence of uranium minerals in Burma is sadly lacking in the available literature but owing to the growing importance of this most strategic mineral with the advent of atomic age, the Government of the Union of Burma has taken steps to remedy this deficiency. The Atomic Energy Centre of the Union of Burma Applied Research Institute is surveying the whole country for the radioactive minerals in general and uraniferous minerals in particular and so far a few indicative discoveries are made although definite economic deposits are yet to be found.

"Uraniferous materials occur in fossil wood and as hematite nodules in an area 3 miles north-east of Obauk village, Magwe District"[1], in the Central Burma but they are a very low grade mineral. Only one or two samples collected around this area gave assays greater than 0.1% U_3O_8 equivalent. "These materials so far discovered form no sizeable deposit to attract economic interest"[1].

Investigation made around Taungdwingyi area indicated occurrence "in fossil logs, in loose sands and in laterite gravels"[2]. There is no sizeable deposit and no attractive concentration of ore. The highest assay figure given by a sample suspected to be a hand picked one is 0.11% U_3O_8 equivalent. Other samples assayed much below this figure.

Besides the above-mentioned areas of Irrawaddian Sedimentary rocks, the Union of Burma Atomic Energy Centre strongly suspects "as a result of field work and laboratory research"[3] the occurrence of uraniferous minerals in the area around Mogok, Shwebo District, in Dawna Range, Karen State, in granite and granite pegmatites of Tenasserim particularly of Mergui district, in area west of Mong Kung, a southern Shan State, and in the old hard rocks on the western edge of the Shan Plateau along the eastern part of Yamethin and Taungoo Districts. The Atomic Energy Centre of the Union of Burma Applied Research Institute is encouraging prospectors, indivi-

dual and otherwise, to direct their attentions particularly to these places.

Thorium

Thorium is "a possible source of nuclear fuel for atomic power; Th_{232} could be converted to the fissionable element U_{233}" [6] which could be used in place of U_{235} in the generation of atomic energy. "The interest in Thorium for this application is due to its abundance in the earth's crust"[6]; it is estimated that thorium is four times as abundant as uranium.

The occurrence of monazite in alluvial deposits has been reported in the Tavoy District, namely at Kyanchaung and Shwechaung, at the area around Kanbauk and in the stream sands and other favourable places in the Heinze Basin. But owing to the general unrest in the country, the investigating party of Atomic Energy Centre could reconnoitre only the Kanbauk area and some places in the Heinze Basin. Monazite is found as "a common mineral associated with cassiterite in the tin alluvials of the Heinze Basin. It is also found as impurities in the tin concentrates". [4] No one has as yet determined the extent of the deposits and no attempt is so far made to recover the mineral although the presence of monazite is confirmed.

In the Mergui District, the occurrence of monazite in small quantities is reported at Shwe Du and Lamawpyin chaungs. They are said to be of no economic interest, but further investigation should be undertaken.

On the reports of monazite occurrence by the prospectors, the Union of Burma Atomic Energy Centre visited the beach around Amherst (at the mouth of Salween River). Although there are no past record on the occurrence of monazite in this area, the investigating party confirmed the reports, saying "it is evident that monazite does occur on the beaches along the Tenasserim coast"[5]. Other economic minerals such as zircon, rutile, ilmenite and cassiterite are reported to occur along with monazite. This is surely a definite indication for serious prospecting and exploitation in the coastal area.

In Mong Kung, Southern Shan States, the monazite occurrence is reported in the sands of a stream flowing past the village of Wan Hapalam.

Beryllium

Beryl is reported to occur as a common mineral in the wolfram and cassiterite lodes of Byingyi in the Yamethin District. It also occurs at Mogoke and in the sands of the Irrawaddy although no one is as yet interested in this mineral. More valuable forms have attracted the attention of the miners. Aquamarine of a sea green and bluish green

colour is found in granite-pegmatite at Sakangyi, near 42nd mile on the Thabeikyin—Mogoke road. "Chrysoberyl occurs at Mogok and neighbourhood but is rare"[8].

Rare Earth Metals

Although the rare earths are found in many minerals, the only significant ores are monazite and bastnasite. As described under thorium, the monazite deposits in Burma are in the Mergui District, Tavoy District, Amherst District and Mong Kung in the Southern Shan States. Although the occurrences of monazite have been confirmed in these places, due to various reasons, economic production has not been started.

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REVIEW OF BENEFICIATION TECHNIQUES PERTAINING TO URANIUM-BEARING ORES

*By G. P. Mathur & P. I. A. Narayanan**

The paper reviews the world occurrences of uranium, discusses the application of physical methods of beneficiation to these ores, and outlines the practice followed in some of the important plants. Saskatchewan and Great Bear Lake regions in Canada, Shinkolobwe mine in Belgian Congo and the Colorado Plateau in the U.S., are the important producers of uranium ore for the non-communist world. Various ore-dressing methods, viz., electronic sorting, electromagnetic separation, heavy-media separation and other gravity methods and flotation, as applied to the concentration of uranium ores, have been outlined. Uranium-bearing ores in general are more amenable to treatment by chemical methods than by mineral dressing methods, as the uranium minerals are usually very finely disseminated in ore bodies and are soft and get slimed easily. Preconcentration of certain types of ores, is however done, where conditions are favourable for elimination of the gangue minerals by ore-dressing methods. The processes employed at Radium Hill, Port Radium, and a few plants in South Africa and France have been briefly outlined.

Until recent years, uranium found few uses and all its requirements were obtained as a by-product from operations for the commercial recovery of such metals as vanadium or radium. The demand for uranium increased enormously since 1945 with the development of atomic energy. Seldom has the progress of mineral discovery for any metal equalled the rate at which new uranium deposits have been found and brought into production in recent years.

In the early days of the urgent demand for uranium, attempts to apply the conventional physical methods of concentration to uranium-bearing ores, revealed difficulties in their application. Existing chemical knowledge was, however, sufficient to suggest that a more speedy answer to the problem of uranium concentration could be obtained by chemical methods. But with the increase in types of ore discovered, and because of the refractory nature of some important uranium-bearing minerals, it has become necessary to devise physical methods of concentration in order that economic chemical treatment can be applied.

It is obvious that the treatment problems are no less complex and varied for uranium than for other metallic ores. Further the problems include features which are unusual for other ores in as much as the uranium minerals themselves are more variable in properties and composition than most other ore minerals.

Types of Ores

Uranium ores are comparatively rare. The primary minerals, like pitchblende, are invariably associated with granitic rocks. The

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secondary uranium minerals, like carnotite etc. are derived from the weathering of primary minerals, and may be found associated with granitic rocks, or they may be water-transported to sedimentary formations. The uranium minerals can be classified into the following three general types : (i) Uraninites; (ii) Columbates, tantalates and titanates of the rare earths & uranium; (iii) Secondary uranium minerals.

The uraninites are the richest in uranium, and include crystalline varieties such as broggerite, cleveite, and nivenite. These varieties occur in pegmatites and often in well-shaped crystals. Pitchblende is amorphous uraninite occurring often in metalliferous veins and is associated with various sulphides, including Ag, Fe, Pb, Co, Zn, etc.

The uranium minerals belonging to type (ii) are of complex chemical composition, often well crystallized, and occur in pegmatite dikes.

The secondary uranium minerals like carnotite, autunite, torbernite etc., are all derived from the alteration or decomposition of primary uranium minerals, and may occur in both igneous and sedimentary formations. The various secondary minerals include phosphates, carbonates, arsenates, sulphates, silicates, and vanadates of uranium.

Occurrences

The important uranium deposits of the world are outlined below.

Australia :

Northern Territory : The deposits and prospects are confined almost entirely to the Darwin-Katherine region. At Rum Jungle, where uranium oxide is being produced, uranium minerals occur in carbonaceous shale. Other deposits in the area are Whites' and Dyson's deposits, South Alligator River area, ABC prospects near Katherine, Coronation Hill and George Creek.

South Australia : At Radium Hill, uranium ore is being mined and concentrated. Davidite is the principal uranium mineral with minor amounts of carnotite.

Queensland : The prospects are confined mainly to the Cloncurry —Mt. Isa region. Davidite is the principal uranium mineral. Brannerite disseminated in carbonate beds and lenses, is found near Mt. Isa. The Mary-Kathleen deposit consists mainly of allanite, garnet and apatite and also contains uraninite and rare earths.

New South Wales : In the Broken Hill district, davidite occurs in one area and in other parts of the district, secondary uranium minerals are found.

Belgian Congo :

The Shinkolobwe mine of Union Miniere du Haut Katanga, has been the principal source of uranium for the non-communist world. About 30 different types of uranium minerals, such as oxides, uranates, urano-silicates, urano-phosphates, urano-carbonates and urano-molybdate, occur in the region. The common occurrence of Cobalt and Nickel as sulphides in association with uraninite is a unique feature of the deposits.

Brazil :

The auriferous zone of the State of Bahia holds conglomerates and gold and arsenosulphide-bearing lodes containing uranium minerals. Uranium-bearing pegmatites containing polycrase, fergusonite, samarskite etc., are found in the State of Minas Gerais.

Canada :

Saskatchewan : The Goldfields region (Beaverlodge) north of lake Athabasca, is the most active uranium area in Canada. Pitchblende is the principal uranium mineral. Gunnar Mines, and Ace area have high grade deposits.

Northwest Territories : The mine at Port Radium near Great Bear Lake, is the largest source of uranium ore production in Canada. The ore containing pitchblende, found near Stark area averages 3.0 to 3.5% U_3O_8, 0.36% Co, 0.30% Cu and 0.23% Ni.

Other areas : Deposits of uraninite and bastnasite are found in the Rexspar region. Herb Lake, Bird River and Rennie regions in Manitoba, Sioux Look-out region in Ontario and Gaspe region in Quebec, have promising deposits of uranium minerals.

The Canadian reserves are estimated at about 225 million tons of ore averaging 0.1% U_3O_8.

France :

The principal uraniferous centres are Mortagne, La Crouzille, Grury and Lachaux regions.

Apart from the uranium-bearing carbonaceous schists of the Schaentzel and uraniferous coal seams of Ronchamp, all the known formations are of the hydrothermal vein type.

India :

The uranium ores of India can be broadly classified into three categories:

Low grade ores disseminated along the copper belt thrust-fault zone of South Bihar: The uranium mineral is probably a primary one

associated with apatite-magnetite rocks, chloride-schists, quartzite etc. The uranium minerals also occur as segregations and disseminations in granitic gneiss forming an irregular belt in the Arvalli series in Rajasthan.

Ores in pegmatites : The uranium minerals are of many varieties; the most important are samarskite, fergusonite, annerodite, davidite, uraninite, pitchblende and their secondary alteration products, uraniferous allanite, triplite, cheralite and monazite.

Deposits of monazite : Beach sand deposits of Travancore in Kerala State contain on an average 1-2% monazite. The monazite concentrates obtained from these beach sands contain about 0.3% U_3O_8. The reserves of monazite are estimated at 2 million tons. Cheralite which carries 4-6% U_3O_8 and 19-33% ThO_2, is present in some of the varieties of monazite sands.

United Kingdom :

The United Kingdom gets its bulk supply of uranium from other countries, particularly from Belgian Congo. However, some deposits have been reported in Cornwall. The uranium minerals consist of metatorbernite, autunite and zippeite with pitchblende as the principal one.

United States of America :

Deposits of uranium minerals in terrestrial sandstone, mudstone and limestone are the largest source of uranium in the United States to-day. They are numerous and widespread from Texas and South Dakota westward to Nevada and California. Uranium occurs in some of the igneous rocks at the Adams Tunnel, Grand and Larimer counties in Colorado. The vein type of deposits are distributed from the Eastern side of Rocky Mountain westward to Southern California and eastern Washington. The principal uranium mineral is pitchblende. Uranium is also appreciably concentrated in some marine carbonaceous shales and in most marine phosphate rocks. Such deposits are distributed from the western limit of the Appalachian Mountains in Virginia, Kentucky, to the eastern front of the Rocky Mountain.

The United States ore reserves with an average of 0.25% U_3O_8 content are estimated at about 60 million tons.

Union of South Africa :

Uranium is found in conglomerates of the Witwatersrand formations and occurs as a mixture of hydrocarbons and pitchblende. To this type of ore, the name "Thucholite" has been given. Daggafontein and Vogelstruisbult on the East Rand are important sources of uranium. The Monarch Reef is the most important of the uranium-producing reefs.

U.S.S.R. and Eastern Europe :

The average grades of urano-vanadium ores in Turkistan are 1.5% U_3O_8 at Tyuya Muyun and 0.12-0.2% at Taboshar and Maili-su. Betafite deposits have been discovered near Lake Baikal and in the eastern Siberia.

Deposits have also been found in Buchove, Kremikovzi and Seslavkzi in Bulgara, Joachimsthal mines in Czechoslovakia and Silesia in East Germany.

Beneficiation

At present only a few plants viz., those at Radium Hill in Australia, Port Radium in Canada, and at a French mine, have been described in which purely physical methods are used for uranium concentration. These include electronic sorting, electro-magnetic separation, heavy media separation and other gravity methods, and flotation.

Electronic sorting :

The Laponite picking belt makes use of the radioactive properties of the uranium-bearing minerals to reject waste below a prescribed grade. This process has been applied to some Canadian ores. Its application is limited to coarse sizes down to about 1 inch. The rejection of waste by this treatment will range from 30 to 40% of tonnage mined.

Electromagnetic separation :

Uraninite and thucholite possess medium magnetic susceptibilities whereas pyrrhotite etc. and those that are partly coated with ferruginous alteration products are relatively more magnetic. When conditions are favourable magnetic separation may thus provide a means of concentrating uraninite. Encouraging results have been obtained by this method from ores from the Carbon Leader (Blyvoornitzicht mine) and from the Kimberlay Reef (East Daggafontein mine) in South Africa, with uranium recoveries of about 73 and 83 percent respectively.

Heavy media separation :

Where uranium minerals are liberated at a coarse size, heavy media separation could be successfully employed. In such cases, the conventional type of sink-and-float should yield satisfactory grades of rejects. For other ores, finer crushing to $\frac{1}{4}''$ or so, may be required in order to liberate the uranium-heavy mineral aggregates and the cyclone type of heavy media separation is often employed for such ores using magnetite as medium. Heavy media process is employed at Radium Hill, Australia, where plus 10 mesh ore is treated using ferrosilicon as medium and the minus 10 mesh undersize is concentrated by flotation.

Other Gravity Methods :

In most of the low grade primary ores, the uranium minerals are finely disseminated requiring fine grinding for their liberation. The secondary minerals, autunite, torbernite, carnotite, etc. are soft and get slimed easily and ores containing such minerals cannot be efficiently concentrated by gravity methods. If the uranium mineral in an ore is the heavy pitchblende, as at Port Radium, Canada, gravity concentration by jigs and tables is possible. When ore reserves permit, it is probable that gravity concentration could be employed for pegmatitic deposits also, where minerals such as uraninite and uranothorite are often well crystallized.

Flotation :

Uranium does not occur as sulphide and therefore, cannot be concentrated by the usual sulphide flotation practice. Flotation, however, is employed to float the associated sulphide minerals with a view to enriching the uranium fraction or eliminating those non-metallic minerals which are undesirable during leaching.

In France, flotation is employed at one of the mines to concentrate uranium minerals, principally parsonsite, a recovery of 85% being obtained without desliming. Alcoholic solution of oleic acid is used as the collector.

At Radium Hill, Australia, flotation is employed to concentrate davidite from the heavy media concentrates and the —10 mesh under size. Anionic reagents used for iron and titanium oxides have been found suitable.

Thucholite from Witwatersrand, South Africa, has responded well to flotation since it is a hydrocarbon mineral.

Physical Beneficiation Practices

As already pointed out, only chemical methods are employed in most cases for concentrating low grade uranium ores. Prior to treatment by these chemical methods, particularly leaching, certain types of ores are preconcentrated to eliminate as much of gangue minerals as possible with some sacrifice in recovery of uranium. Physical beneficiation methods as practised for uranium ores in some countries, are briefly outlined below.

Australia

Radium Hill : Radium Hill ore is the only uranium ore in the world for which an efficient, complete ore-dressing process has been successfully developed. Without this concentration process, the costs of chemical treatment of the run-of-mine ore would have been prohibitive. The chief uranium ore mineral is davidite. Carnotite occurs as a minor constituent. The uranium minerals occur in inti-

mate intergrowth with varying proportions of rutile, ilmenite, hematite, and some magnetite. Bronze biotite and pinkish quartz are the principal gangue minerals.

The run-of-mine ore is crushed to 1½″ size and wet screened over a 10 mesh sieve. The +10 mesh material is pre-concentrated by heavy media separation using ferrosilicon suspension at a specific gravity of 2.83. About 60% of the total feed to the heavy media separation plant is rejected as coarse tailing. The heavy media concentrate, up-graded with a ratio of concentration of 3.5: 1 and with a recovery of about 92%, is crushed and ground for further treatment by flotation. The —10 mesh fraction screened out ahead of heavy media separation is also ground fine and combined with the ground heavy media concentrate for flotation. The rougher flotation concentrate is cleaned and re-cleaned using additional reagents. Diesel fuel, Linseed fatty acids, Peltogen (Sulphonated whale oil) and cresylic acid, are the reagents employed.

Overall uranium recovery in the final concentrate averages 83% with a concentration ratio of 6: 1. The concentrate after thickening and filtration, is sent to Port Pirie for chemical treatment.

Canada :

Eldorado Mining and Refining Ltd., Port Radium : Pitchblende is the uranium mineral in the ore.

The run-of-mine ore after passing over a sorting belt, is crushed to —⅜″+4 mesh, —4+8 mesh and —8 mesh sizes. The first two fractions comprising about 85% by weight, are treated in rougher jigs, and then cleaner jigs to produce marketable concentrate. The tailings are re-ground and retreated.

The —8 mesh product from the above screening constitutes the feed to the fine jig circuit. It is first roughly sized in a hydraulic cone classifier with the sand product forming part of the feed to the jigs. The cone overflow discharges to a Dorr bowl classifier, the overflow from this unit pumped to thickener for dewatering prior to leaching. The Dorr classifier sands are sized in a sizer and the coarse-size product from this forms the balance of the jig feed. Jig concentrates are dried and bagged for shipping.

The jig tailings are dewatered, reground and returned to Dorr classifier circuit for re-sizing and retreatment in the secondary jig circuit. The Dorr sizer overflow is treated in a hydro-classifier. The overflow is pumped to thickeners prior to leaching, and the underflow passes through flotation circuit for recovery of copper. The flotation tailing joins the feed to the leaching plant.

France :

Flotation is employed with good results in two of their plants, although working details of the processes are not available.

(i) In one of the plants the ore is made up of parsonsite crystals, dissminated in quartz gangue. Chalcolite, Kasolite, and various sulphides (galena, zinc blende) are the other accessory minerals. Flotation at a pH of about 7, using a solution of oleic acid in ethyl alcohol gives very encouraging results.

(ii) In another plant the ore is a mixture of pitchblende, chalcolite, autunite, uranotile, parsonsite and pyrite with quartz, feldspar, mica and clays as the gangue minerals. Direct flotation of this complex ore using a mixture of oleic acid, alcohol and Teepol gives good results. pH is critical and is maintained between 6.4 and 7 by suitable addition of sodium carbonate.

Due to the presence of pitchblende and uranotile in the mineral, a combined gravity-flotation method has also given very good results. The yield is about 65% with a concentration factor of 20.

India :

Another paper that is being presented during the symposium deals in some detail with the amenability of Indian uranium ores to physical methods of beneficiation. It may be mentioned that an experimental pilot plant of capacity 200 tons/day is already in operation at Ghatsila in the Bihar Copper Belt to concentrate uranium from the copper tailing employing gravity, magnetic and flotation methods.

Monazite which is a constituent of Travancore beach sands gets concentrated in the non-magnetic residue after removal of Ilmenite. It is further separated from the associated minerals viz., quartz, zircon, sillimanite, garnet etc. by a series of operations employing gravity and magnetic methods, yielding a final concentrate of high grade containing about 0.3% U_3O_8.

Union of South Africa :

Most of the uranium produced in South Africa is obtained by direct leaching of gold tailing, supplemented in a few cases by flotation concentrates from current cyanide residues and slime dam residues of Daggafontein and Vogelstruisbult mines in Witwatersrand region.

Both thucholite and sulphides are important carriers of uraninite. It has thus become possible to recover the uraninite not by itself, but by recovering the constituents with which it is associated. About 75% of the total uranium is recovered from the Carbon Leader (Blyvooruitzicht mine) by successive flotation of thucholite, sulphides and uraninite and its other carriers. Thucholite is easily floated by

the use of a frother only, such as pine oil, with about 20-30% uranium recovery. Subsequent flotation with xanthate increases the uranium recovery by completing the flotation of thucholite and floating some uraninite. The remaining uraninite is finally floated using oleic acid. Further details of the process are lacking.

United States of America

The only plant about which some information is available is situated at Warwick, New York, and operated by Ramapo Uranium Corporation.

Radioactivity is found in lean magnetite, between granite rock and magnetite veins, and the mineral uraninite occurs in and around pyrite. The ore assays 0.05 to 0.15% U_3O_8. The plant uses a dry grinding technique, followed by air separation and magnetic cleaning, which yields a barren sand, an almost barren high grade iron product, and a high grade uraninite and pyrite concentrate assaying 50 to 86% U_3O_8.

Conclusions

In spite of considerable amount of study undertaken towards development of physical benefication methods for uranium-bearing ores, the results in general have not been very encouraging. Flotation of undesirable gangue minerals, such as sulphides, has had some success. Carbonaceous uranium minerals associated with asphaltic ores, and gold-cyanide residues, are readily amenable to concentration by flotation. Other physical methods of beneficiation, such as wet attrition grinding, gravity separation methods, electrostatic methods, etc., have resulted in either low recoveries or low ratios of concentration. It is therefore seen that only a few of the ores being processed for uranium have been found amenable to physical beneficiation techniques, such as ores treated at Radium Hill, Port Radium and a few plants in South Africa and France.

In India, physical beneficiation as applied to low grade uranium ores, is still in an experimental stage with the possible exception of a uranium bearing flotation tailing which is now being tested at Ghatsila in a semi-commercial plant of capacity 200 tons per day.

SOME ASPECTS OF THE DRESSING OF LOW GRADE URANIUM ORES AND BEACH SANDS IN INDIA

*By R. Krishnaswamy**

Uranium occurrences in India are of three types, of which the pegmatite deposits are of little importance. The low grade deposits in the metamorphic rocks present special problems because of the finely disseminated nature of the uranium minerals in them. If the association of the uranium is preferential to one or more of the gangue minerals, a bulk concentration of uranium and the particular associated gangue is possible. In some exceptional cases, direct dressing techniques have also been developed. The highly altered condition of the associated para-magnetic minerals in the beach sands complicate the recovery of monazite. These, however, have been solved in the laboratory by a few alternative methods, and their relative economic merits are under study.

Uranium occurences in India can be grouped into three classes. Of these, those of pegmatitic origin are too sporadic to be economically mined. Some of this ore is produced as a by-product of the mica industry. A major bulk of this production belongs to the 'refractory' type, comprising the columbates, tantalates, and titanates of uranium.

The occurence as fine disseminations in metamorphic rocks, and the placer deposits of monazite in southern and north-eastern India comprise the main bulk of our uranium resources.

The metamorphic rocks in the thrust zone of south Bihar are, at the moment, the most promising of the simple oxide ores of uranium. These ores contain from 0.2 to 2.0 pounds of uranium per ton. The uranium mineral in these ores appears to be one of the oldest minerals to be formed. There is evidence to suggest that uranium mineralization started earlier than the silicates, and continued through the magnetite and apatite epochs. The later formations of sulphides and apatite therefore quite often enclose in them some of the uranium. Even though in some cases fair-sized crystals of uranium minerals have been located, the majority of the activity in these ores is due to fine disseminations, which sometimes are as small as 5 microns.

Since the uranium has been the oldest to be deposited, it has been subjected to all the later attacks from agents of weathering. Where the action has been severe, uraninite has undergone successive oxidation and hydration to yield a wide range of gummites, which, in a number of cases have been pushed into the cracks and fissures in the gangue minerals of the host rock. In places, where hematization of magnetite has taken place, the oxidation of magnetite to hematite has also been accompanied by some of the uranium being absorbed in the newly formed hematite lattice. This has given rise to metamict hematite in these ores.

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The secondary uranium minerals, autunite, and torbernite are often found as surface encrustations, and as loose and flaky deposits along fissures, and cracks. But these, by themselves, form a very minor part of the uranium values in the ore.

Invariably, these ores require a fine grind for liberation. Both because of the inherent fine size of the disseminations, and their low hardness, the uranium minerals in these ores easily tend to slime in grinding, and get concentrated in finer sizes. Table 1 gives a typical uranium distribution in a ball milled material.

Table 1

Size in microns	Weight percent	Assay % U_3O_8	Percent Distribution.
plus 72	48.2	0.015	22.6
72 to 56	1.4	0.040	1.8
56 to 40	6.5	0.014	2.8
40 to 28	8.8	0.021	5.7
28 to 20	8.5	0.029	7.7
20 to 14	6.5	0.030	6.1
14 to 10	6.0	0.050	9.4
minus 10	14.1	0.100	44.0

The dressing methods requiring a coarse grind are generally not applicable to these ores. Radiogenic picking, heavy media separation, and jigging, used elsewhere in uranium milling industry are practically useless to these ores. The shaking table has found some use. Performance of the table depends upon the degree of liberation that is obtainable at a reasonable grind.

But for some notable exceptions among the secondary uranium minerals and some of the ferro-titanium minerals of uranium, flotation has not been found to be highly selective. So far, no specific reagent conditions have been found that show a particularly marked selectivity for the uranium minerals, especially the oxides and the hydrated oxides. Where flotation has succeeded in yielding a high recovery of uranium even though at a rather poor ratio of concentration, the success can be attributed to the fact that the uranium is more closely associated with one or more of the gangue minerals, leaving the others free. The Table 2 shows the comparative results of flotation studies in the case of two ore samples. Both these are from the same deposit, and are mineralogically the same. The sample 'A' was obtained from near the surfaces, where the ore was subjected to weathering action. The magnetic product from this sample, originally assumed to be magnetite, was found on x-ray diffraction studies, to consist mainly of hematite, which was metamict. This may imply the possible existence of at least a small part of the uranium substituting for iron in the hematite lattice.

Sample 'B' was obtained from depth, far below the water table in the area, and not subject to so much of weathering. Here, the magnetite was not hematized, and showed a sharp x-ray powder diffraction pattern, even in the back reflection region. Except for this, the mineralogical compositions of the two were about the same.

Table 2

	Percent weight		Percent U_3O_8		Percent distribution.	
Product.	Ore A	Ore B	Ore A	Ore B	Ore A	Ore B
Feed	100.0	100.0	0.11	0.10	100.0	100.0
Conc.	28.0	26.1	0.32	0.13	84.1	33.8
Tails	72.0	73.9	0.023	0.089	15.9	65.2

The mineral compositions of the products in the above were about the same in both the cases, except for the uranium distribution. It is quite evident that the concentration of uranium in the case of 'A' is quite incidental, and is occasioned by the closer physical association of uranium with the ferro-magnesium group of the gangue minerals. In such cases, a bulk flotation of the associated gangue minerals indirectly effects a fair uranium concentration.

In the case of phosphate minerals of uranium, successful flotation techniques have been developed as a direct method of concentration. However, these do not as yet have any economic application, as the occurrences of these minerals are not large. Where they do occur, they form very thin and friable encrustations of the exposed surfaces, and joint planes of fissures and cracks in the host rock. An autogenous grind, and attrition wash have successfully concentrated most of these.

Flotation, as a direct method of concentration was successfully employed in Australia for the brannerite-davidite-abesite group of minerals. In India, brannerite occurs in Rajasthan, and is associated with clay minerals. The difficulty in applying the flotation technique developed in Australia to the Indian ore is that it requires large quantities of collector reagents, which reduce the froth stability seriously. The clay minerals begin to float indiscriminately, if the froth is stabilized maintaining the collector concentration. With the aim to obviate these difficulties a phase -exchange method was developed, by which recoveries of the order of 90% could be obtained at an enrichment ratio of 18 to 20, in a single stage process. The recoveries and enrichment ratios are extremely good, compared to those usually obtained in dressing practice of low grade uranium ores today. In plants in operation on low grade uranium ores, the enrichment ratios vary from 2 to 5 (in exceptional cases 10), at recoveries from 75 to 20 percent.

The metallurgy of uranium involves a hydrometallurgical stage, irrespective of what the starting material is. The physical dressing me-

thods for uranium minerals do not operate at high selectivities such as are obtained in other non-ferrous milling practices. Since the primary object of dressing is to affect an overall economy in the process, the emphasis quite often shifts from the direct enrichment of the uranium mineral to the removal of those gangue minerals which adversely affect the economics in the hydrometallurgical stage. Thus, the removal of carbonates and phosphates commonly occurring in the host rock, and which consume acid in the leaching process, becomes necessary. Similarly, if an alkaline leach is to be used, the removal of pyrite and other sulphides becomes essential.

Both apatite and pyrite, the commonest of the undesirable gangue minerals, which consume leaching reagents, are easily floated off by standard well known methods. However, the flotation of apatite quite often involves a fair amount of uranium loss in the apatite concentrate. The usual fatty acids and soaps which float apatite also tend to float part of the oxide of uranium. So far, no selective depressing agents for uranium minerals have been developed. The indiscriminate flotation of uranium with apatite is controlled to a certain extent if the froth consistency is closely controlled.

The third source of uranium is the placer deposits of monazite in southern and north-eastern India. Travancore sands contain from 0.5 to 3.0 per cent monazite, which in turn contains about 0.3 to 0.4 percent uranium. The associated minerals in the raw sand are ilmenite, quartz, sillimanite, zircon, rutile, garnet, and traces of a few other zirconium, thorium, and uranium oxide minerals. The beach sands have been mined and processed for well over twenty five years. When the industry started, ilmenite was the main product, monazite being a relatively unimportant by-product. The process consists essentially of magnetic and gravity separations. Even now, with the greatly increased stress upon the importance of monazite, the economics of the industry depends largely upon the efficiency of ilmenite and rutile concentration This presents a considerable difficulty from the ore dressing point of view. The ilmenite is a considerably altered product, representing various stages of differential removal of iron from ilmenite, ultimately resulting in rutile or brookite. The whole series of altered products between the two end members is collectively named leucoxene. It thus represents a rather hetrogeneous substance composed of phases of highly different magnetic susceptibility. In the magnetic separation the behaviour of an individual grain of this altered ilmenite will therefore depend upon its magnetic susceptibility.

The alteration of ilmenite is often accompanied by the creation of voids in the individual grains due to the obvious dislodging of parts therefrom. Because of these voids, the apparent specific gravity of these grains also varies very considerably, thereby varying the behaviour of leucoxene in gravity processes. If a high recovery of titanium minerals is attempted, it results in their contamination by monazite because of the wide range of their magnetic susceptibility. Some grains of

leucoxene are always such that they have similar magnetic susceptibility as that of monazite, and the contamination occurs during the magnetic separation. This also reduces the possible monazite recovery. Thus, the leucoxene is a problem both in ilmenite recovery and in monazite concentration. Electrostatic separation may be used to effect a better separation between monazite and the titanium minerals. All these minerals usually have a salt coating on them, as they are sea-water deposits, and this decreases the degree of discrimination in an electrostatic field. A fresh water wash to remove the salt coating, and subsequent warming up of the sand to nearly 65 to 70°C helps the separation greatly. Even then the separation requires a number of repeated operations.

A method has been successfully developed for the easy separation of leucoxene from monazite, involving a magnetizing roast to increase the magnetic susceptibility of the former. In the grains of leucoxene there is invariably a certain amount of free hematite formed during the alteration of the ilmenite. This is easily converted to magnetite in a reducing roast. However, this requires roasting at 600°C.

A successful flotation process has also been developed for monazite. The early experiments were conducted with imported cationic reagents. For a good selectivity, amines or amino acetates with at least ten carbon atoms were found necessary. The grade of monazite depends to a large degree upon the froth consistency, which was controlled in the early experiments by aero-froth reagents. Work undertaken in cooperation with the Sri Ram Technical Institute, Delhi, has resulted in developing a locally synthesised reagent from coconut oil. This has shown a remarkable selectivity for monazite, and produces almost pure monazite concentrate at better than 95 per cent recovery, when used with aluminium sulphate and sodium silicate as conditioners. The relative economics of these processes is yet to be worked out.

The beach sands also contain sillimanite. This was at one time produced and marketed by the Travancore Mineral Company and has since been given up due to a number of reasons. A flotation technique for the concentration of this has also been developed in the laboratories of the Trombay Establishment.

The main difficulty in the concentration of silimanite is to depress the zircon, which has a tendency to float with it. This is overcome by the controlled use of oleic acid with sodium carbonate and sodium silicate instead of the costlier sulphonated hydrocarbons used elsewhere.

The placer deposits of north-east India, like the Travancore deposits, contain ilmenite, rutile, quartz, garnet, and small amounts of zircon, in addition to monazite. They also contain fair amounts of magnetite which is not normally found in Travancore deposits. This ilmenite is not so highly altered and is easily picked up in low intensity fields. The monazite also shows a greater magnetic susceptibility than that in the Travancore sands. The general grain size of this sand is usually larger

than of its counterpart in Travancore. These deposits have not yet been thoroughly studied for their dressing characteristics. The indications are that the problems mentioned earlier in connection with the Travancore deposits will not exist.

Discussions

Dr. V. A. Altekar, (*Dept. of Chemical Technology, Matunga, Bombay*): Since the uranium minerals are generally characterised by their friability and tendency to slime, it may be worthwhile to consider such recovery processes as are generally adopted in the case of friable and heavy minerals like the tungstates or cassiterite.

I would be interested to know if equipment like Frue Vanners or the Buckman tilting tables or blanket surface were tried out to recover slimy uranium minerals.

Reference has also been made to the difficulty of magnetically separating partially weathered minerals like leucoxene with ilmenite core in them, so that their magnetic response is similar to that of monazite. Could not a process using surface properties like flotation or electrostatic separation be used with advantage? If necessary electrostatic separation may be improved by selectively coating surfaces of one mineral or the other.

Author's Reply: We have tested a deck similar to one used in Buckman table, which was found useful in the treatment of cassiterite. As, however, this test was done on one ore only and that too not fully, we cannot generalise. Our finding on these tests, however, is that this is not very useful.

Leucoxene is a heterogenous material with variable voids, and cores of possibly the original or partly altered mineral. Some of leucoxene grains are similar to monazite in magnetic susceptibility. There is no difficulty in its electrostatic separation from monazite. The only pretreatment that would be desirable is a fresh water wash. In the industry where the electrostatic separation is preceded by wet gravity separation in fresh water, the separation is sharp.

Dr. R. Caillat, (*Atomic Energy Commission, France*): I thank the speaker. I may here mention that though there are some methods generally used for upgrading minerals, ores which come from each particular mine do call for special methods of treatment.

THE EXTRACTION AND RECOVERY OF URANIUM FROM AUSTRALIAN ORES

*By T. R. Scott**

Prior to 1944, uranium ores were mined principally for their radium content and uranium was a by-product used mainly in the ceramic industry. In Australia, two deposits had been worked sporadically in this fashion—that at Radium Hill, which was discovered in 1906 and that at Mt. Painter, also in South Australia, which was discovered in 1911. The latter deposit consisted mostly of autunite and torbernite and was thus the easier to process, but the former was of interest because the high titanium content of the ore led to attempts to produce titanium oxide pigment as an additional by-product. Unfortunately, the presence of chromium and manganese caused slight discoloration of the pigment, sufficient to militate against the success of the project, but the experience gained on the field was to prove of considerable value in later years, when the uranium content of the mineral davidite present in the ores became the important feature of the deposit. The early work on both these deposits has been described in detail by Thomas[1].

In 1944, when supplies of uranium were urgently required for military purposes, attention was again directed to the Mt. Painter deposits and a simple leaching process was devised in the Division of Industrial Chemistry laboratories of C.S.I.R.O. for extraction of uranium from the ores, while various chemical precipitation methods for recovery of the uranium from solution were tested on a laboratory scale[2]. The urgency of this work became less at the conclusion of World War II and further investigations were also discouraged by the relatively unfavourable results of extensive drilling operations on the field. Meanwhile, attention had been redirected to the titaniferous uranium ores of Radium Hill, firstly at C.S.I.R.O. with regard to their titanium content and subsequently on the geological side by the South Australian Department of Mines, which believed that the lode system might be sufficiently extensive to justify the development of the field as a uranium deposit. During the years 1948-51, in conjunction with other work, several novel processes were developed in the C.S.I.R.O. Division of Industrial Chemistry for the recovery of uranium from Radium Hill ore and these were subsequently tested on small pilot plant scale when it became apparent that the deposit merited development solely as a source of uranium. In 1952, the South Australian Department of Mines set up Research and Development Laboratories to supplement their facilities, and investigations on the chemical treatment of Radium Hill ore thereupon passed from C.S.I.R.O. to South Australia, together

* of Division of Industrial Chemistry, C. S. I. R. O., Melbourne, Australia.

with a nucleus of senior research personnel with extensive experience in the treatment of uranium ores.

During this period, the Australian Government had been active in encouraging prospecting for uranium, with the result that in 1949, a major discovery of uranium ore was made at an abandoned copper prospect at Rum Jungle, in the Northern Territory. Samples of the ore, which contained both pitchblende and a variety of secondary minerals (especially phosphates), were extensively tested, both at C.S.I.R.O. Division of Industrial Chemistry and at overseas laboratories, and a leaching and recovery process was devised to suit the ore. Pilot plant investigations were conducted in cooperation with the South Australian Department of Mines, with such success that production started at Rum Jungle on full plant scale in the later months of 1954. Towards the end of the same year, production of flotation concentrates also started at Radium Hill[3] and, in 1955, the production of chemical concentrate from this difficult material was commenced at Port Pirie, South Australia[4].

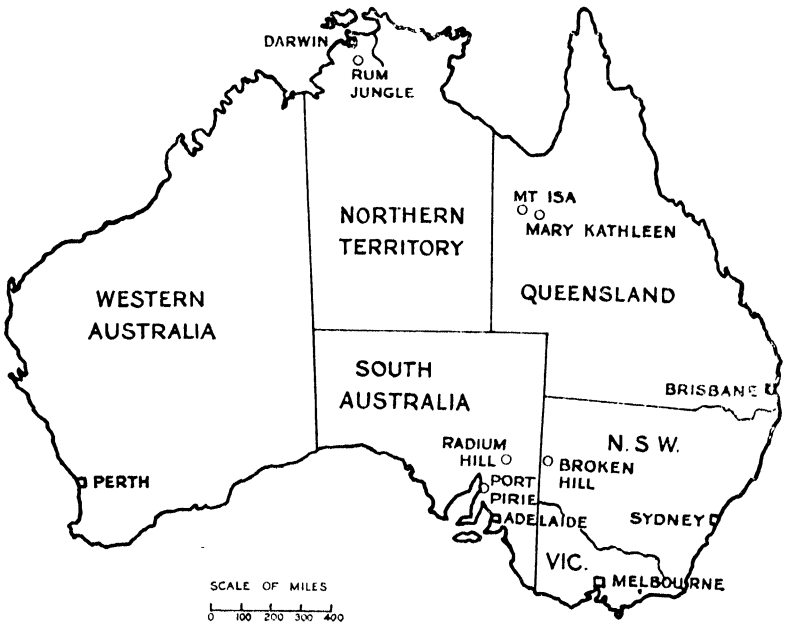
Largely as a result of these activities, Australia experienced a boom in uranium mining especially during 1954, and a number of smaller deposits were discovered in the Northern Territory, some of which now supply ores to the Rum Jungle plant for chemical processing. At least one of these deposits, El Sharana, owned by United Uranium N. L., is also currently producing a saleable uraninite concentrate by gravity ore-dressing methods and reserving the tailings for chemical treatment. Many of the recent finds in the Northern Territory are spectacular but of unproved extent and occur in difficult and remote locations. However there seems no reason why major discoveries should not be made as investigations at depth are prosecuted.

Many radioactive occurrences were also located in north-western Queensland during this period, but it was left to a taxi-driver and spare-time prospector at Mt. Isa in Queensland to make the major discovery. This was the Mary Kathleen deposit[5], 40 miles east of Mt Isa, which was found in 1954, subsequently sold for £250,000, with a controlling interest acquired at a later stage, by Rio Tinto Ltd. The orebody is unusual,[6] in that it is a skarn mineralization with apatite, garnet, allanite and stillwellite[7] preponderating. Among the associated minerals uraninite is dispersed throughout the orebody and is the predominant uranium mineral, except in the surface layers where secondary minerals (e.g. uranophane) preponderate. It is proposed initially to mine this hill of ore by open-cut methods, although future development will depend upon the extent in depth of the uranium-rich ore.

The major ore-bodies so far discovered all occur in the Pre-Cambrian portion of the continent, which comprises the western and central part of Australia. It seems that the eastern boundary of this area constitutes the most rewarding area for uranium discoveries; certainly,

uranium finds in the Palaeozoic and later deposits are few and far between, and generally confined to minor occurrences associated with granitic emplacements. No major deposits have been found to date in Tasamania, Victoria, New South Wales, Eastern Queensland, or Western Australia, despite extensive air surveys of selected regions in some of these States, organised by the Commonwealth Bureau of Mineral Resources.

It should be stated here that the Commonwealth Bureau of Mineral Resources has been instrumental in conducting the majority of the air searches for uranium throughout Australia, assisted by ground parties of geologists and geophysicists operating at favorable localities. Preliminary examination of ore samples has been widely spread, with Commonwealth services supplied by the Bureau of Mineral Resources and the C.S.I.R.O. Mineragraphic Section at Melbourne, and supplemented by the individual efforts of the Mines Departments and Mining Companies in the various states, with especially extensive investigations by the Mines Department of South Australia.



With the establishment, in 1953, of the Australian Atomic Energy Commission, a greater degree of coordination has been achieved in the development of uranium resources in Australia. Not only are contributions made towards the training of the necessary scientists, but grants are also made to university departments to encourage investigations into the treatment of local ore deposits. The Commission itself does not deal, except by proxy, with the processing of ores, but is

interested in co-operating with such organisations as undertake this work and, in general, in supervising the mining and exploration activities throughout Australia. Although the main work[8] of the Commission is to develop the experience and the techniques necessary for the proper utilization of the fissionable materials obtained in Australia, including the setting-up of atomic reactors, the use of radio-isotopes, etc., it also buys uranium ore under previously stipulated conditions from Australian producers and collaborates with Territory Enterprises Pty. Ltd., a private company which acts in a managerial capacity to produce uranium for the Commission from the Rum Jungle deposits.

The historical outline given above suffices to describe what has happened up to the present date in Australia with regard to exploitation of the known uranium deposits. In the sequel, a description will be given of the modes of operation of the major uranium-producing plants and of some of the investigations which have been undertaken on laboratory scale in connection with general processing problems.

Plant Operations

Of the major deposits currently known in Australia, two are actively engaged in supplying ore for chemical treatment. A third, at Mary Kathleen in Queensland, is due to start production of chemical concentrate in the latter part of 1958. An outline of the processes at these three plants is given in Table 1, supplemented below by details for each deposit and by an account of recent development regarding newer sources.

Table 1 : Processing of Uranium Ores in Australia

	Rum Jungle	Radium Hill	Mary Kathleen
Through-put of ore (Long tons/day)	200 (nom)	90†	1000
Leaching			
96% H_2SO_4 (lb. per ton ore)	200-300	750	150
100% MnO_2 (lb. per ton ore)	20-40	Nil	v. small*
Temperature (°C.)	50	Boiling	40
Time (hours)	8-16	10	8
Operation	Batch	Batch	Continuous
Agitation	Air in pachucas	Mechanical plus steam injection	Mechanical
Filtration and/or Washing	Rotary filters	C.C.D.	C.C.D.
Recovery	Absorption on anion exchange resin at pH 1.5-1.7. Elution with approx. $^{M}/_{1}$ NaCl + $^{M}/_{10}$ H_2SO_4		
Purification	Nil	Precipitation at pH 3 with $CaCO_3$	as for Radium Hill
Precipitation	Magnesia addition to pH 6.5-7.0		

† Representing concentrate from 450 tons of Radium Hill ore.

(i) *Rum Jungle* : At least five uranium prospects occur at Rum Jungle[9], the majority being of hydrothermal origin and closely associated with the carbonaceous slates and graphitic schists of the Pre-Cambrian Rocks Creek group. In the major deposit (White's), uraninite is finely disseminated in the host rock, thus precluding simple ore dressing procedures, and is associated with sulphides of copper, cobalt, bismuth, lead and nickel in varying proportions. At Dyson's deposit, nearby, secondary phosphates of uranium (e.g. salecite, sklodowskite, autunite) predominate, except in depth, where pitchblende has been identified.

Although the plant was originally designed to treat White's ore, custom ores from smaller outside mines are also being delivered for treatment after purchase by the Australian Atomic Energy Commission. As a further complication, the ore from Dyson's deposit is physically different from that found elsewhere at Rum Jungle, and special procedures have been found necessary to cope with the clay-like matrix associated with this ore. Although the general procedures on plant scale have already been described[10], some additional comments will be given below to supplement what has already been published.

The temperature of leaching cited in Table 1 is indicative of the climatic conditions in the tropical area at Rum Jungle, even allowing for the heat generated by adding concentrated acid to each batch of ore at the start of the leaching period. The time of leaching is mainly controlled by plant operating schedules and includes holding time prior to filtration. Nevertheless, quite good leaching results may be obtained on a laboratory scale with shorter leaching periods. Oxidant is consumed not only by uraninite, but also by ferrous iron and sulphide minerals, and the amount varies according to the source of the ore. It is interesting in this connection that the secondary uranium in Dyson's ore is leached as well in the absence of oxidant, although the soluble iron is mainly in the ferrous state.

Filtration on large rotary drum filters is satisfactory for the crushed shale and schist constituting White's ore, but breaks down badly for the clay-like ores from Dyson's deposit. The problem here is not to get a suitable residue cake for discharge (which can be achieved by the use of guar gum, Separan, glue, etc.) but to ensure adequate washing-out of soluble uranium from the cake. Owing to the poor settling properties of fines from Dyson's ore, C.C.D. does not represent a satisfactory process for producing liquors suited to static ion-exchange column techniques. Recently, an entirely different approach has been made to the problem by testing the C.S.I.R.O. resin-in-pulp procedure, which can recover uranium from a pulp from which the sands have been previously removed.

Because of the high cost of nitric acid and nitrates in the Northern Territory, salt plants have been set up locally to supply sodium chlo-

ride as eluant from the anionic resin columns. Various schedules of split elution have been employed to reduce the cost of neutralization to pH 6.5-7.0 with magnesia, the latter being a technique suggested by C.S.I.R.O. to produce a more readily filterable uranium concentrate. With proper control, the magnesia concentration of the precipitate can be reduced below 5 per cent. MgO on dry weight of U_3O_8. Special washing procedures have had to be introduced to reduce the chloride content of the product below specification limits. At the time of writing, an enquiry is also in progress to devise methods for reducing the phosphate content of product below 1 per cent. P_2O_5, since the ores from Dyson's deposit can produce as much phosphate as uranium in pregnant liquor, no matter what variations in leaching technique are employed. It appears that a choice will eventually have to be made between chemical precipitation of phosphate from pregnant eluate with ferric iron [11] and solvent extraction of the eluate with 2-ethyl hexyl phosphoric acid, which acts predominantly as a selective solvent for cations, such as uranium.

Equipment at Rum Jungle consists almost exclusively of rubber-lined mild steel, wherever contact is likely to be made with acid, and chloride solutions. An exception is made for filters, which are constructed of type 316 stainless steel.

An interesting by-product is copper, which is either recovered by cementation with iron from the barren liquors or, in the case of undissolved copper sulphides, recovered from washed, spent residues by flotation and sold as such. Very approximately, one quarter of the copper in the ore is dissolved during leaching and recovered as copper sponge. In general, the copper content of White's ore is at least ten times the U_3O_8 grade.

(ii) *Radium Hill* : At Radium Hill, a number of deep and steeply-dipping lodes occur, containing, over an average width of 4 ft., an aggregate of heavy black minerals, including, besides davidite, ilmenite, rutile, magnetite, hematite, pyrite and chalcopyrite intergrown in quartz and biotite. This material, after mining, is concentrated by heavy-media separation and flotation to yield a product of nearly ten times higher grade than run-of-mine ore and one which has proved economic to transport 202 miles by rail to the chemical processing plant at Port Pirie. Details of the mine and ore-dressing plant have been described elsewhere[3].

At Port Pirie[4], uranium is dissolved from the concentrates by a boiling leach with sulphuric acid, using conditions which result in a low concentration of titanium in the final liquors. The idea of using relatively dilute acid for recovering uranium from the ore was first conceived at C.S.I.R.O. as early as 1949 and represented a radical departure from previous schemes. The prolonged leaching period is efficacious in ensuring substantially complete precipitation of titanium from solution, in order to avoid later troubles in the course of ion-

exchange operations. No oxidant is required, since ample ferric iron is dissolved from the concentrates to ensure a suitably high redox potential in the liquors.

After dilution with water and pH adjustment with lime to 1.5-1.7, leach liquors are recovered by counter-current decantation in a series of rubber-lined thickeners, and passed after clarifying to standard ion-exchange columns. Uranium is desorbed, as at Rum Jungle, with acidified sodium chloride (1.0M) and pregnant eluate is precipitated in two stages to recover uranium concentrate. A slurry of lime is added to pH 3.0-3.2 to remove iron (and calcium sulphate) and the purified liquors, after settling, are precipitated with caustic magnesia, as at Rum Jungle. This variation in technique results from the much greater solution of iron in the processing of Radium Hill concentrates, leading to appreciable absorption of iron on the resin columns and to subsequent serious contamination of the pregnant eluates, unless two-stage precipitation is used.

Equipment at Port Pirie varies from one part of the plant to another. For the digestors, mild steel containers are lined with acid-resisting tiles, but the agitators are of stainless steel. Both lead-lining and polyvinyl chloride piping are used in subsequent stages, with the exception of the thickeners (see above).

Since the concentrates from Radium Hill contain, in addition to major amounts of titanium, significant amounts of vanadium and rare earths (with a most unusual distribution[12] of the latter), there is ample scope for production of elements other than uranium at a later date, both from the leach liquors and the residues. Such investigations will doubtless be prosecuted by the South Australian authorities at the appropriate time.

(iii) *Mary Kathleen* : Although the plant at Mary Kathleen is not expected to be in operation until late in 1958, most of the flow-sheet detail has been frozen and can thus be described at this early stage. All the necessary processing investigations were carried out by the South Australian Department of Mines, including testing at pilot- plant scale.

The essential feature of the leaching process is that apatite must be protected from acid attack, otherwise acid consumption is at least quadrupled and re-precipitation of phosphates of uranium and the rare earths tends to occur during and after leaching. The laboratories of the South Australian Department of Mines were responsible for demonstrating that these difficulties could be overcome by a continuous leach, with acid addition controlled so that the leach liquor pH did not fall below 1.6. This principle has subsequently been applied by C.S.I.R.O. to other phosphatic ores occuring in Australia, with no improvement in the case of Dyson's ore (Rum Jungle) and with great success for apatite-containing ores from the South Alligator River area

of the Northern Territory, which moreover responded favorably over a pH range extending from 1.3 to 1.9. The essential feature of these experiments is that, with a suitable grind of the ores, uraninite should be readily and relatively selectively leached, in only a few hours, at the constant pH selected. Because of the different leaching procedure suggested for Mary Kathleen, it is unlikely that the leach pulp will reach the same temperature as at Rum Jungle, but only an approximate figure can be given in view of the lack of full scale operating data.

In general, oxidant is not needed for the ore, except to control the ferrous iron concentration as affected by the metallic iron introduced during grinding. Some pyritic bodies occur in the ore, however, and small additions of oxidant may be needed to ensure that the redox potential is suitable for leaching of the uranium minerals with such ores (hence asterisk in Table 1).

The dense ore at Mary Kathleen responds very favourably to washing by counter-current decantation and no difficulties are anticipated at this stage. Recovery of uranium from pregnant liquors will be undertaken by the conventional static-column system, with sodium chloride elution, as for the ores mentioned above.

Since the ore-body at Mary Kathleen is a rare-earth metasomatism, substantial quantities of rare earths (mainly of the cerium group, thus differing from Radium Hill) will be available in either the liquors or the residues. Boron, from the new mineral, stillwellite[7], is also an intriguing constituent. It is too early, however, to decide what extraneous materials may be recovered as by-products from this deposit, since full-scale operations have not yet been commenced.

(iv) *South Alligator River, N. T.* (*see map*) : Very recently, reports have been received regarding developments with a variety of deposits in the above area, located in rugged country near Darwin, N.T. It appears that ores from United Uranium N.L. (which has already been described as a source of gravity concentrates) may be processed in a new chemical plant, for which details are not yet available. It is tentatively proposed that a solvent extraction process will be used to follow one of the conventional acid-leaching procedures, using ethyl-hexyl phosphoric acid as the solvent and stripping with sodium carbonate after each extraction cycle. Whether this process will prove to be competitive or not with the new C.S.I.R.O. resin-in-pulp technique is not known, but developments will be awaited with interest. On the leaching side, the ores are generally amenable to the current Rum Jungle processes, with uraninite occurring at depth and a variety of secondary minerals in the more superficial materials.

(v) *Anderson's Lode* (*Counter Lease*), *Queensland* : This deposit came under notice in 1954, at much the same time as Mary Kathleen, but has been given less consideration because the constituent minerals,

which include apatite, calcite and ferromagnesians such as sphene, biotite and chloride, are so soluble as to make acid-leaching a precarious operation. Under alkaline leaching conditions, results obtained at C.S.I.R.O. were no more favorable. However, in the Australian press ("Age" 4th Oct. 1957), mention is made of an agreement between an Australian and a Canadian Company to treat the ore by a new process, on the assumption that some 800 tons of U_3O_8 are available in the deposit on present known reserves.

(vi) *Other Deposits* : Along the South Alligator River area, N.T., and extending to the western border of Queensland, various other deposits have come to light which have considerable promise if a reasonable amount of ore can be revealed. Transport costs in this area prohibit much movement of ore unless it is of high grade, hence the attempts to produce saleable uraninite by physical methods of ore dressing on site. Nevertheless, the tailings from these operations should still be worthy of consideration, and, in the absence of specific processing problems, should be available for such processing plants as may become available in the vicinity.

Laboratory Investigations

In association with overseas organisations, which have been approached on various occasions to help with processing problems, Australian laboratories have always been in the forefront regarding the evaluation of plant procedures for Australian ores. Laboratory investigations at various locations have been encouraged by the Australian Atomic Energy Commission, which does not itself undertake work of the type described in this paper. Initially, no attempt was made to apportion work of specific types to the laboratories available for consultation, but a pattern has naturally developed over the course of a few years.

The C.S.I.R.O. laboratories of the Division of Industrial Chemistry in Melbourne have continued to act as consultants on processing matters to the Atomic Energy Commission. Samples of ores from new deposits are submitted for examination and custom ores near a purchasing point (e.g. in proximity to Rum Jungle) are aubmitted for evaluation to determine whether or not they are amenable to processing at the Rum Jungle plant. This is because of a provision in the Atomic Energy Act which enables the Commission to reject ores, irrespective of grade, which would need special and separate treatment[8]. Data on mineralogical or ore-dressing aspects are available from the appropriate C.S.I.R.O. sections also located in Melbourne. As a research institution, the Division of Industrial Chemistry has also been enabled to undertake investigations on new processes or on problems which, although prospective, had not arisen in practice at the time of initiation. Some of these will be mentioned in the sequel and have represented a distinctive and important contribution by C.S.I.R.O. in this field.

The Research and Development Laboratories of the South Australian Department of Mines were set up in 1952 to investigate problems asso-

ciated with any of the mineral deposits of that state, but the emphasis was naturally laid on uranium in the early stages. Complete co-ordination is provided here between the ore-dressing, mineralogical, chemical and pilot plant aspects of the processing of a particular ore and most of the uranium producers in Australia have availed themselves of these services at some time or another on a paying basis. The Radium Hill deposits represented a special case, being located within the state, but pilot plant assistance was also given to Territory Enterprises Pty. Ltd. in the development of their Rum Jungle plant and the complete process for the Mary Kathleen deposit was also worked out in South Australia.

At a later stage, a "development" group was instituted at Rum Jungle, especially to solve problems arising or foreseeable on the plant scale, but also to investigate new procedures which might prove worthy of full-scale development. Much useful work has already been done by this group, which works to some extent in collaboration with C.S.I.R.O., e.g. in instances where fundamental laboratory scale investigations appear to be desirable.

At the University of Queensland, investigations have been started on the ore from Anderson's Lode (Counter Lease) near Mt Isa, and will undoubtedly prove helpful in view of the recent decision to produce uranium concentrate from this deposit.

Some of the problems which have been or are being investigated will be noted below. The list is not meant to be complete, since the author is understandably less familiar with some of the newer projects being studied outside C.S.I.R.O.

(i) Production of uranium metal

Work has been in progress for some time on this subject in South Australia, with a view to producing suitable material for reactors from the uranium concentrate made at Port Pirie.

(ii) Recovery of uranium by resin-in-pulp techniques

C.S.I.R.O. have patented[13] the application of continuous counter-current movement of resin through ore pulps of up to 50 per cent. solids. The column procedure is believed to be superior to alternative resin-moving processes and has already been proven on Mary Kathleen ore[14], despite the high density of this material. It is believed that current pilot scale tests on a difficult material, viz. Dyson's ore from Rum Jungle, will establish the efficacy of the technique on a permanent basis.

(iii) Pressure leaching

With the object of using the sulphide minerals in Rum Jungle ore as an autogeneous source of acid, investigations into pressure leaching with air and water as the sole reagents were instituted at C.S.I.R.O. in

1953. However, it quickly became apparent that basic knowledge in this field was deficient, and much of the work up to the present has been devoted to the development of adequate laboratory apparatus and to the elucidation of the kinetics governing the decomposition of various sulphide and primary uranium minerals. With certain ores (e.g. Dyson's ore at Rum Jungle), pressure leaching even in the absence of sulphide, is of value in increasing the yield of soluble uranium.

(iv) Solvent extraction

On the assumption that solvent extraction is ultimately the most acceptable recovery process for uranium on plant scale, constant attention has been given to new developments in this field, especially with regard to amine and alkyl phosphate extraction from sulphate solutions. The use of tributyl phosphate as extractant, necessarily from nitrate solutions, has been given especial attention, in view of the favourable properties of this reagent for plant scale operations. Since success in this project depends on an inexpensive source of nitric acid (which cannot otherwise compete with sulphuric acid), many procedures for the cheap regeneration of nitric acid from stripped nitrate leach liquors have been examined, including ion exchange, electrolysis with selective membranes, thermal decomposition, distillation, etc.

(v) Purification of uranium product

Various specifications have been drawn up to control the quality of uranium oxide sold from chemical processing plants. Apart from undesirable contamination by chloride and sulphate, phosphate content has been the major problem in some instances. C.S.I.R.O. have described[11] a simple precipitation at pH 2.9-3.0 on pregnant eluate, which is capable of reducing phosphate contamination below specification limits, using ferric iron as a selective precipitant. Alternative procedures, using solvent extraction towards the same end, have also been investigated.

It is not proposed to specify in further detail the wide variety of other problems which have been examined by Australian laboratories. While assistance from agencies outside Australia is always welcomed and has been freely availed of, it is a source of gratification that satisfactory solutions to the majority of problems have been obtained by plant and research groups within Australia.

Summary and Conclusions

An account has been given of the development of the uranium industry in Australia, with emphasis on the wide variety of sources from which information and services have been and still are available. Sufficient data have been supplied to indicate the nature of the plant and chemical procedures adopted by the major producers of uranium oxide, although it is outside the scope of the paper to describe all plant flow sheets in detail.

It is apparent that Australia is already a significant producer of uranium product and has the potential to become a major producer in the course of time. The success of Australian research and development groups in the past is a good augury for future progress, not only in the production of uranium from new or difficult deposits, but also for the utilization of by-products from the various ores to ensure a continued supply of uranium at a competitive price.

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General (a) "Some Problems in the Development of Atomic Power" Symposium (October 1954) Melbourne University.
(b) "Atomic Power in Australia" Symposium (September 1954) N.S.W. University of Technology.

Discussions

Mr. B. H. Krishna, (*Atomic Energy Establishment, Bombay*) : I refer to the report of Dr. Scott on the development of a modification of the currently used R.I.P. process. It is said that this provides not only continuous counter-current extraction of uranium but also works with a pulp with as high as 20% solids of — 325 mesh secured by a simple sand-slime separation of the acid leach. The thin pulps mostly employed in R.I.P. contain about 4-5% solids of -325. I wonder if the comparatively high solid content of the pulp may not cause trouble in settling, depending on the retention time with the counter-current resin mass. Is it possible that the character of the ore is such that little or no tendency to settle exists in the leach solids? Otherwise if the intention is to use a simple sand-slime separation to separate — 325 from + 325, it may be necessary to add a suspending agent to maintain the pulp with uniform flow characteristics. However, I do not see any particular value in maintaining such a high pulp concentration unless the separation of a large proportion of — 325 presents a problem. But if a smooth flow can be achieved with other slimes, that would be of particular value in dealing with some of our low-grade ores. I am also not sure of the effect of abrasion in pulps of such high solid content. The consequent resin losses may be quite serious. Could Dr. Scott provide any further information on the working of the process?

Author's Reply : In the instance mentioned the ore used was from Dyson's deposit, Rum Jungle. This material slimes very badly during leaching. To avoid undue dilution, — 325 mesh pulps at 20% solids were used successfully. No settling occurred in the column and no suspending agent was required. In fact the settling properties of the ore for C.C.D. purposes are so poor that it would probably be uneconomic to use this technique to produce a clean liquor for static ion exchange colums. The viscosity of the pulp incidentally was so high that heating to 40-50°C was found desirable to reduce the viscosity to a workable value.

Smooth flow at 20% solids has also been achieved with Mary Kathleen ore, which is denser than most ores. No settling problems were encountered at the flow rates used.

Prolonged tests are necessary to measure abrasion losses. Experience up to date indicates that such losses should not be serious. Much depends on obtaining good smooth spherical beads of resins to start with.

Mr. D. V. Bhatnagar, (*Atomic Energy Establishment, Bombay*) : From the leach liquor containing phosphate obtained from Mary Kathleen ore, what process do you propose to use to win the uranium?

Author's Reply : The leach liquor from Mary Kathleen ore is not expected to contain much phosphate, since the leach is conducted continuously and at a controlled pH (1.6) where apatite is relatively little attacked. Consequently, the standard static ion exchange column will be used for absorbing uranium with elution using M/1 NaCl + M/10 H_2SO_4. Pilot tests have shown good loadings and a satisfactory P_2O_5 value on final concentrate.

Mr. D. V. Bhatnagar, (*Atomic Energy Establishment, Bombay*) : What in your opinion is the most efficient eluting agent for eluting uranium from the resin bed loaded with uranium and phosphate?

Author's Reply : Ammonium nitrate acidified with nitric acid is the most efficient of the commonly used eluting agents. Sodium chloride, acidified with sulphuric acid comes next and sulphuric acid alone at similar strength comes last. This order is, to the best of my knowledge, followed whether phosphate is present or not.

The choice of eluting agent is generally based on cost e.g., nitrate eluant is practised in South Africa but chloride eluant is used in Australia.

Concluding **Dr. Caillat** remarked that only the specialists in this field are aware of the difficulties which they have to overcome and so many problems may be discussed in detail outside the symposium.

PROBLEMS IN THE LEACHING AND EXTRACTION OF INDIAN LOW GRADE URANIFEROUS ORES.

By J. Shankar and B. H. Krishna.*

ABSTRACT

The main problem encountered in the hydrometallurgy of the Indian low grade uranium ores is due to the presence of a number of reagent consuming minerals e.g., apatite, pyrite, etc. The paper also discusses some of the factors which effect the economic processing of these ores.

The large deposits of Indian uraniferous ores usually contain uranium ranging from 0.01% to 0.1% U_3O_8. The deposits in the thrust zone of Bihar appear to contain the primary mineral uraninite or pitch-blende finely disseminated in the metamorphic rock except in the upper layer where some transformation has occurred and the flaky secondary minerals, autunite and torbernite are found. The other associated minerals vary to some extent from one location to another. Table I gives the mineralogical and chemical analysis of two of the typical ores of this zone.

Table I—Mineralogical and chemical analysis of ores from the thrust zone of Bihar.

	E-87	E-130
Mineralogical:		
Quartz and felspar	41%	46%
Chlorite and Biotite	44%	30%
Apatite	4%	3%
Magnetite, hematite and limonite	5%	10%
Tourmaline	traces	6%
Pyrites	2%	1%
Ilmenite	1%	1%
Others	3%	3%
Chemical:		
SiO_2	58.6%	61.2%
Fe_2O_3	5.2%	7.5%
Al_2O_3	10.8%	9.9%
TiO_2	0.55%	1.2%
MnO	traces	traces
CaO	2.2	1.5
MgO	4.9	3.4
P_2O_5	1.5	1.0
U_3O_8	0.012	0.06
S	0.9	0.24
Loss on ignition	2.9	2.6

The other large deposit from this part of the country discovered last year is that of monazite which, like the well-known placer deposits

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of Travancore on the west coast, contains 0.3% to 0.4% U_3O_8. Full particulars are not yet available but indications are that this may turn out to be even larger than the already known ones.

Another area where occurrences of uranium have been reported is Rajasthan. The U_3O_8 content of these is somewhat higher than those of the Bihar ores. The primary uranium mineral here also appears to be uraninite which is not so finely diffused in the host rock. Table II gives the composition of two typical samples from this area.

Table II—Mineralogical and chemical analysis of ores from Rajasthan.

	E-129	E
	%	%
Mineralogical :		
Quartz, felspar	60	58
Muscovite		30
Chlorite, biotite	22	..
Apatite	1	1
Magnetite, hematite and limonite	9	3
Tourmaline		5
Others	8	3
Chemical :		
SiO_2	58.6	
Fe_2O_3	10.7	
Al_2O_3	14.8	
TiO_2	1.1	
MnO	0.1	
CaO	0.7	
MgO	3.5	
P_2O_5	0.16	
U_3O_8	0.18	0.30
S	absent	
Loss on ignition	4.3	

The present paper will deal with the leaching problems of the low grade ores containing minerals such as pitchblende, uraninite, autunite etc., to the exclusion of minerals such as monazite, samarskite, fergusonite.

Leaching

The first step in the hydrometallurgy of uranium consists of digestion of the finely ground ore or ore concentrate. In the primary mineral, uranium is essentially in the reduced state while in the secondary minerals it is present in the partially or almost completely oxidised state. The primary minerals pitchblende and uraninite and the secondary minerals such as autunite, torbernite and carnotite are amenable to both acid and alkaline carbonate-bicarbonate leaching. The choice of the process depends to a large extent upon the interference of the gangue minerals and to some extent on factors such as reagent costs, material of construction, oxidation needs and recovery methods available.

The chemistry of uranium is fairly well-known. An acid solution dissolves the oxide of uranium forming the soluble uranyl salt:

$$UO_3 + H_2SO_4 \rightarrow UO_2SO_4 + H_2O$$
$$UO_2 + H_2SO_4 + 1/2O_2 \rightarrow UO_2SO_4 + H_2O$$

A carbonate solution likewise dissolves the oxide as the soluble uranyl carbonate complex :

$$UO_3 + 3Na_2CO_3 + H_2O \rightarrow Na_4UO_2(CO_3)_3 + 2NaOH$$
$$UO_2 + 3Na_2CO_3 + H_2O + 1/2O_2 \rightarrow Na_4UO_2(CO_3)_3 + 2NaOH$$

The sodium hydroxide produced in the above reactions will precipitate the solubilized uranium as sodium uranite or diuranate,

$$Na_4UO_2(CO_3)_3 + 4NaOH \rightleftharpoons Na_2UO_4 + 3Na_2CO_3 + 2H_2O$$
$$2Na_4UO_2(CO_3)_3 + 6NaOH \rightleftharpoons Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O$$

unless sufficient bicarbonate is present in the solution to neutralize the hydroxide ion. This explains the need to have some bicarbonate always present in the carbonate solution for leaching uranium.

The above equations also indicate that the hexavalent uranium contained in the minerals readily gets solubilized in acids or carbonate solutions but for the tetravalent uranium it is essential to use suitable oxidising agents.

In the case of most Indian ores, samples from the surface yield readily to acid or carbonate leaching but those from deeper strata, which are not weathered, need an oxidant to solubilize all the uranium. In certain cases some secondary minerals, like autunite and torbernite, are found as thin surface flaky scales and also in the minute crevices of the ore. These readily yield to dilute acid attack—indeed much more readily than the primary mineral. The acid leaching generally gives higher uranium recoveries compared to the carbonate leaching but the product liquor in the case of the latter is purer, since the reaction of uranium with carbonate resulting in the formation of a soluble complex is rather more specific whereas the dilute acid attack results in a large number of gangue minerals going into solution at the same time.

With very low grade material like the bulk of the Indian ores, leach liquors are rather dilute—indeed too low in uranium content to give satisfactory uranium recovery by the conventional alkali precipitation method.

Some work on the strongly anionic static-resin-bed separation of uranium from carbonate leach liquors has been carried out in the Establishment[2]. The method appears to be very satisfactory. Since however acid leaching yields higher recoveries, many of the existing plants

in various parts of the world are based on the strongly basic ion exchange resin separation from acid liquors.

The ion exchange separation from sulphuric acid solutions is based on the fact that these solutions contain, in addition to the uranyl sulphate molecules and the uranyl and sulphate ions, small quantities of the anionic complex $UO_2(SO_4)_2^{--}$ and $UO_3(SO_4)_3^{---}$ which are absorbed on the anion exchange resin. The mechanism of absorption has been explained in a number of papers from U.S.A. and U.K. presented at the last Geneva Conference and published in many scientific journals during the past few years.

It has been pointed out earlier that the low grade ores found in Bihar and Rajasthan contain varying amounts of apatite and sulphide minerals—pyrites and chalcopyrites. The removal of the latter by flotation without appreciable loss of uranium values, has not presented any serious problem. This has not been so with apatite. In some cases removal of apatite by flotation involves a loss of 10—15% of uranium values. Leaching the ore with dilute sulphuric acid (5—10% v|v) has in most cases resulted in solubilization of the phosphate. Even when the bulk of phosphate is removed by flotation, some remains behind and comes into solution. The effect of the presence of phosphate in leach liquors on the absorption of uranium on the resin and its elution was therefore studied.

Since uranium forms an anionic phosphate complex, it is strongly adsorbed on the resin. Indeed the uranium loading from acid solutions containg phosphate is greater than from the sulphate solution but its elution is more difficult and a larger number of bed volumes are required to recover all the uranium. Also if the acid concentration is low, the uranyl phosphate may precipitate out in the resin bed and cause difficulties. These results are being published shortly.

Problems arising in the leaching and extraction of the low grades ores so far do not appear to be very special to our country. Similar problems are reported to arise also in the exploitation of richer deposits which form the raw materials for uranium production elsewhere. But in addition to the difficulties inherent in the economic utilisation of Indian deposits due to their low grade, they also present other problems.

Most of these ores have no other recoverable values generally. Therefore, they have to be exploited only for their uranium content. At the same time, they contain considerable amounts of both apatite and pyrites which greatly increase reagent costs in any leaching—either acid or carbonate. In some cases, the apatite content is large enough perhaps to warrant its separation and recovery as a commercial product whose value and the consequent reduction in acid cost for leaching, would neutralise partly or entirely the cost of removal.

Preliminary concentration of the ores would obviously be most desirable to reduce the capital cost of leaching and extraction plants

and the reagent costs. But attemps at beneficiation of ores carried out so far show losses of 15—25% of uranium with increase in the grade of the ore by only a small factor[3].

When fed with a concentrate, the capital cost on plant for leaching and later processes will be reduced, compared to the requirements for direct leaching. However, other requirements like grinding mills, handling equipment and services will remain practically the same. In addition, a concentration unit will have to be installed.

The cost of acid for leaching will be reduced roughly proportionately to the reduction in bulk. But cost of operating a concentration plant will be an addition to other costs and will depend on whether a flotation or a gravity process is adopted.

The following factors will have to be taken into consideration in deciding on either direct acid leaching of the ore without concentration (after separation of apatite, if necessary), or after preliminary concentration :

1. The cost of the ore and the grade.
2. The loss of uranium during concentration.
3. The cost of reagants in the preliminary flotation of apatite and in leaching.

It would be seen that while grinding mills and all other facilities remain the same, the reduction of capital cost on plants for leaching and recovery (including ion exchange or solvent extraction) and for treatment and disposal of effluent, will not be proportionate to the reduction in bulk. The labour and supervision charges are likely to remain the same.

If the ore is to be mined at high cost, and operations are on a comparatively small scale, the difference in costs is of a marginal nature. The quantity of uranium equivalent to the losses during concentration may be substantial in relation to the total cost, in which case, direct leaching may be resorted to.

In this connection, the decision of the South African mining industry to adopt generally direct leaching, in spite of the heavy capital cost of the leaching, is of interest[4]. Production of uranium in larger quantities was preferred against losses of uranium through concentration. Where the grade of the gold tailings was very low, e.g., 0.007%, a flotation process concentrating about five times to 0.035% but with a recovery of about 35% was adopted[5].

A careful consideration of local factors is, therefore, necessary in deciding on whether direct leaching of the bulk of the ore or of a concentrate from a preliminary beneficiation may be adopted.

In the acid leaching of low grade ores, the cost of reagents per ton of U_3O_8 produced, especially sulphuric acid (Rs. 170|ton ex-works), assumes considerable importance. Especially in India, due to lack of transport facilities, it may be necessary for the leaching plant to produce its own sulphuric acid. Though the cost of production may compare favourably with acid bought from a distance, it would be of definite advantage if the use of acid is eliminated entirely or substantially reduced. In this context, the adoption of a pressure hydrometallurgical process[6] appears to be of particular interest. The low grade ores hold good quantities of sulphidic constituents, especially pyrites. At the same time, considerable amounts of apatite present will consume any quantity of acid formed *in situ*, thereby increasing the soluble phosphates in the leach liquor. Preliminary flotation of apatite, which is not always simple, is therefore necessary. The treatment of the ore (or its concentrate) by steam and oxygen under pressure, if necessary with additional quantities of pyrites, may possibly dissolve out the uranium minerals existing in low concentration much more quickly than from richer ores. Or perhaps, ore structure influencing the size of the particle, may require the same contact time to dissolve irrespective of its concentration in the ore. Degree of comminution may be expected to have profound effect on the rate of dissolution.

Provision of process steam at fairly high pressure and in large quantities, the use of special and costly materials of construction in autoclaves to overcome severe corrosion conditions and consequent increase in maintenance are the disadvantages. The reduction in the time of leaching, and thereby of the capacity of the pressure equipment, enabling costlier materials of construction being employed, higher extraction efficiency and possibly complete elimination of the use of acid, and therefore of the cost of the acid plant, are favourable factors.

Thus, pressure hydrometallurgy of uranium may prove to be of distinct value in the exploitation of certain types of low grade ores in India, especially those in which comparatively large quantities of copper is also associated[6]. In these cases again, preliminary flotation for concentrating uranium at least five to six times, without loss of copper, is desirable. Investigations of the process for recovery of substantial part of uranium values accompanying comparatively larger copper values, without affecting at least the present efficiency of commercial copper recovery, would be of considerable value in reducing cost of uranium from such sources.

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Discussions

Dr. B. C. Kar (*National Metallurgical Laboratory, Jamshedpur*) : For the solubilization of uranium in quadrivalent state suitable oxidants are to be added. What are the oxidants that are economically used? Is it possible to use air at atmospheric pressure.

What are the relative economics of chemical precipitation including chemical and electrolytic reduction, ion exchange process (RIP and columnar) and the solvent extraction process?

Authors Reply : Oxidant used is pyrolusite in most countries. In Canada, chlorate is used in some of the mills. It is also possible to use air as oxidant in suitable cases, but not at atmospheric pressure.

In many cases precipitation method is preferred, whenever possible. If the uranium concentration is below 2.5 g/litre recoveries by NaOH precipitation are low. However, it appears that ion-exchange and solvent-extraction processes would be better. Of these the latter is now superseding the ion-exchange in certain countries. The solvent and the resin can both be used over and over again. The details are available in the literature. The length of service also depends on the composition of the leach liquor. Dr. Scott perhaps might throw some light on the economics as he has experience of plant operation.

Dr. T. R. Scott (*Australia*) : This question cannot be answered in general terms, but only in relation to a specified uranium ore. All the procedures mentioned have been used on a commercial scale at some time or other. Chemical precipitation is of more use when the pregnant liquors contain considerable uranium, since residual solubility of the precipitate then becomes insignificant. Electrolytic reduction is more costly than that achieved by Fe or Al, but avoids contamination of the liquors with the reducing agent.

Ion exchange has been proved for very dilute acid leach liquors in South Africa and should be equally useful for dilute alkaline liquors, thus filling a role in which chemical precipitation fails.

The "jigged bed" process has been shown by CSIRO (Australia) to be economically superior to static column operation (the latter with clarified leach liquors) for several widely different types of ores. Solvent extraction is in all probability the coming process, because of its flexibility and simplicity on plant scale. The writer favours especially those processes which work satisfactorily with (relatively) high-acid leach liquors, since recycling of the barren liquors with their residual acidity

can thus be achieved. Such a process requires dry grinding and crushing (e.g., with an "Aerofall" Mill) or the dewatering of wet-ground ore after grinding has been completed. Solvent extraction can be employed either with sulphate leach liquors or (using tributyl prosphate as extractant) with nitrate liquors. The latter process would be the ideal if cheap regeneration of nitric acid from barren liquors could be achieved.

Dr. P. P. Bhatnagar (*National Metallurgical Laboratory, Jamshedpur*) : I would like to ask if any information is available on the chlorination of uranium ores. I am of the opinion that chlornation of uranium ores by HCl gas may yield very interesting results, there would be no contamination by silica, etc., and the process may be economic where acid leaching is practised.

Author's Reply : We have not tried hydrochlorination. Chlorination with chlorine gas has been tried on monazite and the results will be shortly published.

THE RECOVERY OF URANIUM FROM ACID LEACH LIQUORS BY ANION EXCHANGE

*By T. V. Arden**

The use of ion exchange resins for the recovery of uranium from sulphate leach liquors has been one of the more interesting contributions of chemistry to the mining and metallurgical industries. In a period of only eight years, it has grown from the laboratory scale to become an established process in large scale use at mines all over the world.

The original observation on which the process is based was made independently at the laboratories of the Dow Chemical Co. Pittsburgh. U.S.A., and the Batelle Memorial Institute, who showed that anionic uranyl phosphate complexes could be absorbed by strongly basic anion exchange resins. Workers at the Massachusetts Institute of Technology, U.S.A., and the Chemical Research Laboratory, Teddington, England applied this observation to liquors obtained from the South African gold ores, finding that anionic sulphate complexes were equally well absorbed. A combined team from Gt. Britain and the U.S.A. set up the first small scale columns at the Western Reefs mine, Transvaal, in co-operation with workers of the Government Metallurgical Laboratory in August 1950.

The results of this work[1] showed that a practical recovery process for uranium has been found. The uranium complex was selectively absorbed, giving a high resin loading in spite of competition from high concentrations of the ions in solution; and elution in the form of a rich and relatively pure solution was readily achieved using M ammonium nitrate solutions. It has since been shown that many other salt solutions may be used.

Following pilot scale tests at two South African mines, the first full scale plant was brought into action in 1952; and the building of new units continued without interruption until this year. The construction programme is now complete, uranium recovery units being installed at 19 mines, with a total production of 6,000 tons U_3O_8 per year.

From South Africa, the process was rapidly extended to other uranium-producing countries. Plants have been installed at Rum Jungle and Port Pirie, Australia, and also in other parts of Africa; but no production figures have been published. Two mines in France, Ecarpiere and Bessines, are using the ion exchange technique. The French production has been announced[2] as 600 tons U_3O_8 in 1958, rising to 3,600 tons by 1975.

The Canadian construction programme, which has been the largest of

* Chief Metallurgist, The Permutit Co., Ltd., London.

all, is nearing completion; and when full production is reached late next year, the output will be 14,500 tons U_3O_8 per year.

In the U.S.A., where there are 12 uranium mills, operating a number of different recovery processes, 8,000 tons U_3O_8 were produced in 1957[2]; and it is probable that at least half this quantity was derived from ion exchange recovery. The latest user of the process is Sweden whose production at present is small—around 10 tons per year—but according to recent announcement, scheduled to be brought up to 120 tons within some years. Although it is difficult to estimate the total world output with accuracy, it seems clear that at least 40,000 tons/year U_3O_8 will be produced by the ion exchange process when the present construction programme is complete.

A considerable amount of research has been carried out on many aspects of the subject; but many of the results are unpublished, and have been recorded only in special reports, whose existence is not widely known. Reviews of many of these have been given by American[3-5], British[6] and South African[7-10] workers.

The Mechanism of Uranium Absorption

It has been shown by Ahrland[11], that uranyl sulphate solutions contain, in addition to cationic uranyl compounds and undissociated uranyl sulphate, minor concentrations of the anionic complexes $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$. Both these compounds are capable of being absorbed by anion exchange resins, their relative proportions being governed by the mass action equation (1) (in which co-efficients are neglected.)

$$\frac{[UO_2(SO_4)_3^{4-}]R}{[UO_2(SO_4)_2^{2-}]^2R} = K\frac{[UO_2(SO_4)_3^{4-}]S}{[UO_2(SO_4)_2^{2-}]^2S} \quad \ldots.(1)$$

Since the total ionic concentration on the resin is constant, it is clear that increasing concentration in solution favours the absorption of the divalent ion, and increasing dilution that of the quadrivalent. It has been shown[12], that in the case of solutions containing less than 0.05M UO_2SO_4, the quantity of the lower complex absorbed is negligible. The absorption of the higher complex of resins in the chloride and sulphate forms is given in equations (2) and (3).

$$UO_2SO_4 + 2SO_4^{2-} \rightleftharpoons UO_2(SO_4)_3^{4-} + 4RCl \rightleftharpoons R_4UO_2(SO_4)_3 + 4Cl^- \quad (2)$$

$$UO_2SO_4 + 2SO_4^{2-} \rightleftharpoons UO_2(SO_4)_3^{4-} + 2R_2SO_4 \rightleftharpoons R_4UO_2(SO_4)_3 + 2SO_4^{2-} \quad (3)$$

While (2) represents a simple exchange process, (3) can be re-written as an addition reaction

$$UO_2SO_4 + 2R_2SO_4 \rightleftharpoons R_4UO_2(SO_4)_3 \quad (4)$$

It is probable that both types of mechanism can occur in practice, and it has been shown[13] that when the uranium complex is absorbed by a

chloride form resin, the chloride is first replaced by sulphate, after which the uranium is taken up more slowly. This process is shown in Fig. 1.

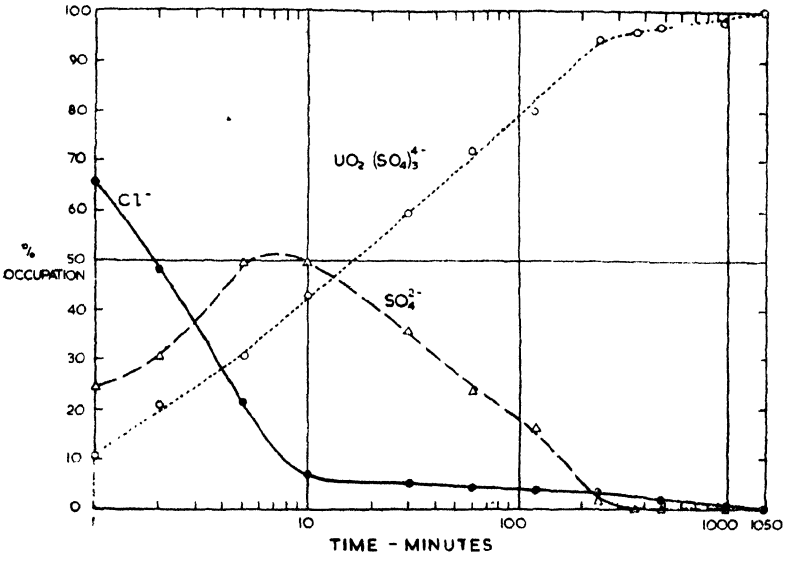

Figure 1.—Absorption at pH 1.86

In addition to the mono-uranyl complexes, condensed complexes are formed at pH values above about 2.0. The uranyl cation hydrolysis according to equation (5)

$$2UO_2^{++} + H_2O \rightleftharpoons U_2O_5^{++} + 2H^+ \qquad (5)$$

and the condensed ion $U_2O_5^{++}$ has been shown[12] to give the anionic complexes $U_2O_5(SO_4)_2^{2-}$ and $U_2O_5(SO_4)_3^{4-}$. As a result, the absorption of uranium increased rapidly with pH, as shown in Fig. 2. In practice, however, it is rarely possible to take advantage of this effect, since leach liquors always contain ferric ions which precipitate at about pH 2.0, and prevent the pH being raised above this point.

Competition from other ions

Leach liquors obtained from the attack on uranium ores can contain a large number of other anions, which may be divided into four types.

(a) *Simple anions.* Those commonly present are sulphate, bisulphate, phosphate, fluoride (when the ore includes fluoride minerals), chloride and nitrate (resulting from the recycling of eluting solutions into the pregnant circuit). All of these ions, which are considered in more detail below, have lower affinities than the uranyl complex.

(b) *Anionic metal complexes.* Of the metals commonly present in

solution, Cu, Al, Fe^{++}, Co, Ni, Zn, Mn, Cr, and Mg do not form anionic complexes which are absorbed to any significant extent. Fe^{+++}, Mo, Th, and V which are absorbed by the resins are considered below.

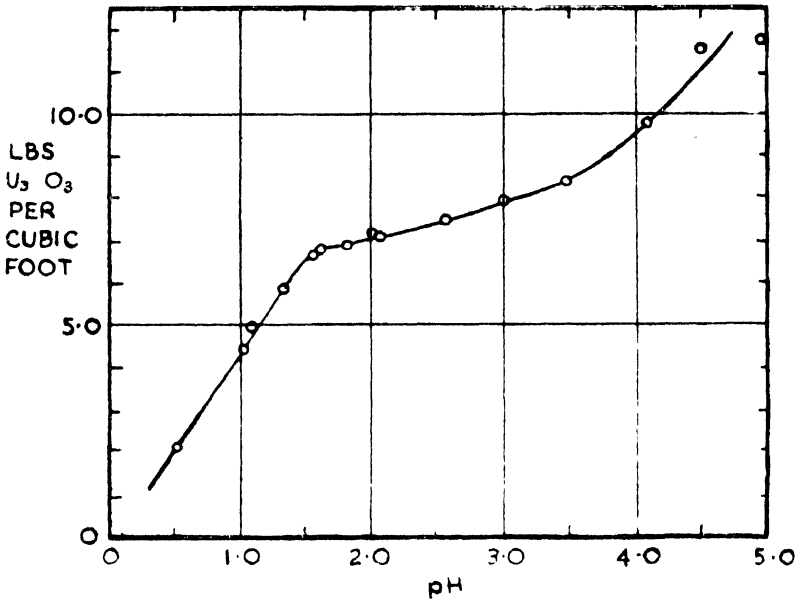

Figure 2.—The absorption of uranium from pure solution by de-acidite FF

(c) *Polythionates.* Many uranium ores contain sulphide minerals, which give rise to traces of polythionate during the leaching process. These ions have higher affinities than the uranium complex, and will displace it from the resin.

(d) *Cyanide complexes.* These are not of general occurrence, but are found only in the treatment of the Witwatersrand gold ore residues. Many of them are held very firmly by the resins, and can cause poisoning.

(e) *Physical poisons.* These include metal oxides, phosphates and silica.

(f) *Organic poisons.*

Simple Anions

Sulphate : If the addition mechanism of equation (4) is correct, it is clear that the SO_4^{2-} ion will not compete with uranium; and it has been shown[12] theoretically that the same result is to be expected from an exchange mechanism. The uranium loading should therefore be independent of sulphate concentration. In practice, this is found to be true over a wide range of concentrations. Fig. 3 shows the variation of $\times UO_2(SO_4)_3^{4-}$ (the proportion of the resin capacity occupied by

uranium) with the measured sulphate content of the solution. This value includes both SO_4^{2-} and HSO_4^{2-}, and it has been shown[12] that the values of $\times UO^2(SO_4)_3^{4-}$ below 1.0 are due to competition from the HSO_4, not the SO_4^{2-} ion. At pH 2.5, when the proportion of HSO_4^- ion is low, the uranium loading is almost constant.

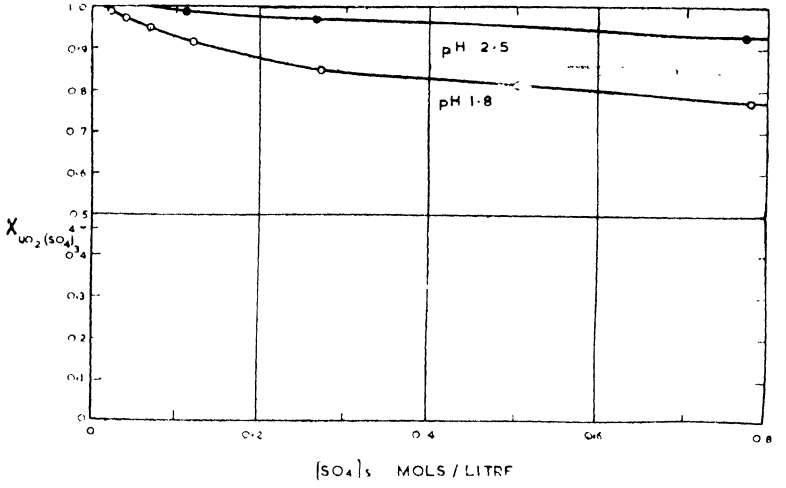

Figure 3.—Composite U-Zr fuel element before extrusion.

Bisulphate : The rapid reduction in uranium loading below pH 2.0 (Fig. 2) is due to the increasing effects of the HSO_4^- ion. In industrial practice, if the liquors resulting from leaching are of low pH, it is advisable to raise this value to 1.8, preferably using for this purpose slaked lime or ground limestone, in order to remove part of the bisulphate by precipitation as calcuim sulphate, while converting the remainder to sulphate in solution.

Fluoride, Chloride and Nitrate : The effect of these ions on the absorption of uranium by De-Acidite FF was tested, using solutions containing 0.7 g|l U_3O_8 and 20 g|l SO_4 at pH 1.8, with the results given in Table 1. In the absence of other ions, the saturation loading was 71 g|l U_3O_8.

TABLE 1.

g|l	% reduction in loading		
	F	Cl	NO_3
0.25	21	5	5
0.5	31	8	—
1.0	51	12	14
2.0	—	22	—
4.0	—	37	43

The interference by fluoride is very marked, which is in contrast with the findings of Wheaton and Baumann[14] that this is one of the least strongly held of all ions. The effect of fluoride must therefore be to complex the uranium in solution, rather than to compete in the normal way. In natural leach solutions, the presence of aluminium and ferric iron, which forms preferential fluoride complexes, can reduce or eliminate fluoride interference. For example, a solution containing Al 0.8, Fe^{+++} 2.1, Fe^{++} 1.0, Th 0.25, U_3O_8 1.3 and SO_4 5.0 g|1 at pH 1.6 gave a resin loading of 68 g|1. The addition of 5 g|1 F to this solution reduced the loading to 62 g|1, a loss of only 7%.

Chloride and nitrate, in concentrations of less than 1.0 g|1, do not cause serious interference with uranium uptake. Thus the concentrations of chloride likely to be present in the natural waters used for leaching are unlikely to cause difficulties. However, during the fractional elution process, it is normal to return the first fraction, which is high in sulphate, and low in uranium, to the leach circuit, while the second, rich uranium fraction, is sent to precipitation. If, by mistake, the cut is made too late, liquors containing high concentrations of chloride or nitrate can become mixed with the pregnant solutions. These liquors can cause considerable desorption of uranium unless they are returned to the leach circuit at a point where they are diluted with a large volume of pregnant liquor.

Phosphate : The case of phosphate is a special one. It does not interfere with uranium loading, since an anionic uranyl phosphate complex is also strongly absorbed by the resin. Elution of this complex is, however, more difficult than that of the sulphate complex, and large volumes of solution are required. In addition, since the solubility of uranyl phosphate is low, there is a tendency for this compound to deposit in the pores of the resin from the concentrated solutions formed during the elution process, unless the acidity of the eluent is maintained at over 0.5N. Fig. 4 shows the elution curves measured, using an eluent containing 0.9M $NaNO_3$ and 0.1 M HNO_3 (total 62 g|1 NO_3), with a retention time of 16 minutes. The original leach liquor had contained 14.5 g|1 Fe^{+++}, 0.1 g|1 Fe^{++}, 11.8 g|1 Al^{+++}, 7.8 g|1 Mg^{++}, 0.51 g|1 U_3O_8, 5.0 g|1 PO_4 and 133 g|1 SO_4 at pH 1.85 ; and the fully loaded resin contained 65.1 g|1 U_3O_8, 107 g|1 SO_4 and 7.4 g|1 PO_4. Precipitation occurred in all fractions up to 7 B.V. and the total quantity of eluent required was 13 B.V. In the absence of phosphate, resin having a similar uranium loading would require only 8 B.V. under the same conditions. When phosphate-containing liquors are treated, a proportion of the phosphate is always found in the rich eluate, and in the uranyl hydroxide precipitated from it. As this ion can interfere with the later processing of the uranium concentrate, it is best eliminated by adding excess ferric nitrate to the eluate, and recipitating a mixture of ferric phosphate and hydroxide at pH 3.5, before the uranium precipitation step. Alternatively, the uranium concentrate can be converted to sodium diuranate, by reaction with excess sodium hydroxide, giving a solution of sodium phosphate.

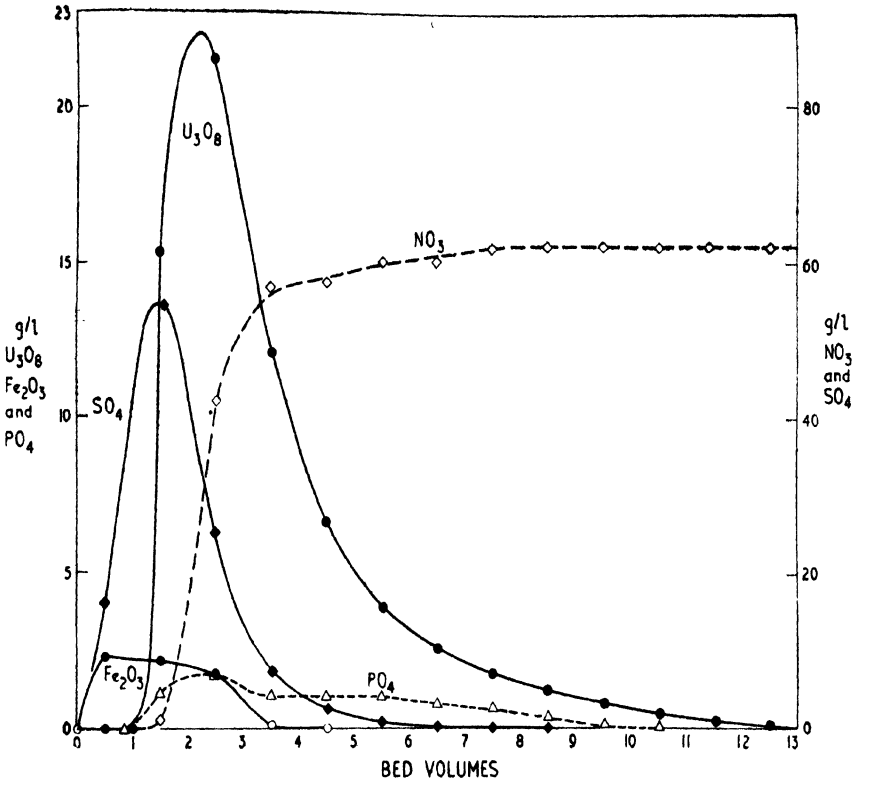

Figure 4.—Elution of de acidite FF after absorption from phospate-containing.

Anionic Metal Complexes

Ferric Iron. The nature of this complex has not been determined, and it is probable that more than one anionic compound exists[15]. The ferric anions have lower affinities than uranium ions for the resin, and in addition, their absorption falls off rapidly with decreasing pH, probably because they are basic compounds of the type $FeOH(SO_4)_2^{-}$, which are unstable in acid solution. Fig. 4 shows the effect of pH on the absorption of uranium and iron from a solution in which Fe^{+++} : UO_2^{++}=23 : 1. At pH 1.3, the ratio on the resin is 0.5 : 1, corresponding with a weight ratio of only 0.1 : 1. Thus in leach liquors containing high concentrations of Fe^{+++}, it is advisable to maintain pH values of 1.2-1.4, in order to obtain the maximum purity of the uranium product.

The values given in Fig. 5 are equilibrium figures. A typical absorption curve is given in Fig. 6. The resin first becomes saturated with iron, which is then displaced by the uranium, so that resins which have not reached equilibrium contain higher iron concentrations.

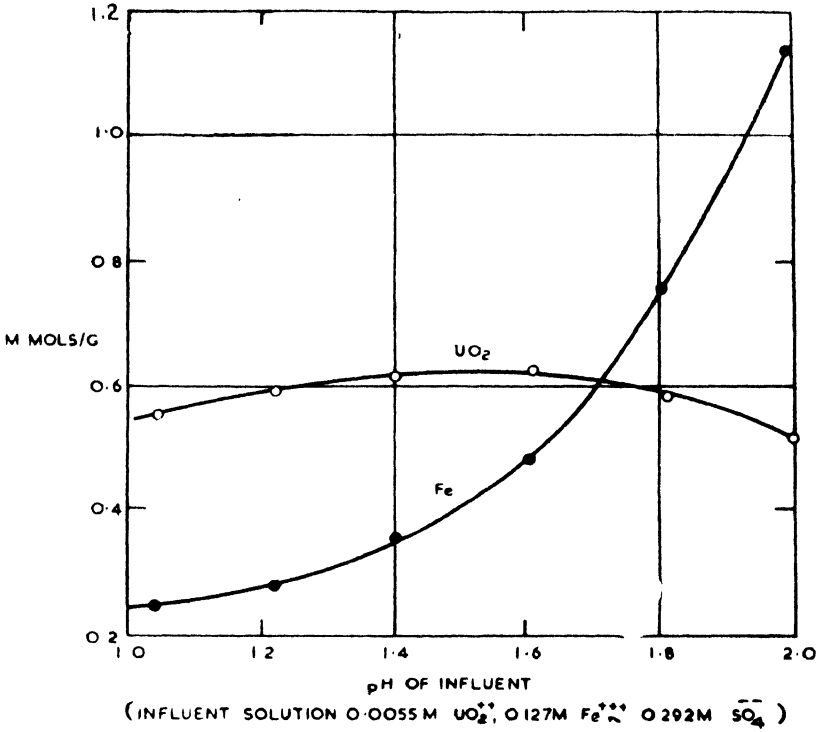

Figure 5.—Effect of pH on Fe and UO_2 absorption.

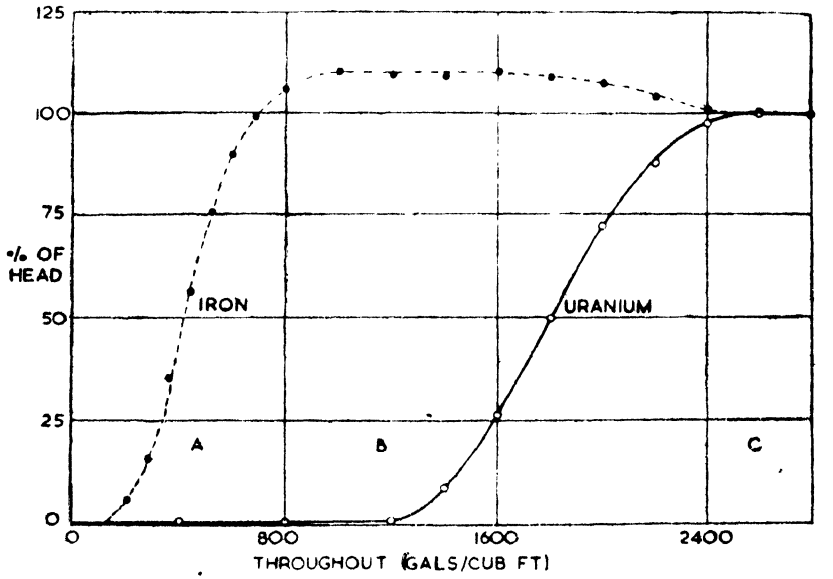

Figure 6.—Absorption of uranium and ferric iron.

It is thus essential to operate columns so as to achieve complete saturation of the resin. The design and operation of columns to give this result are considered below.

Vanadium : Pentavalent vanadium, which is found in liquors obtained from carnotite ores, is readily absorbed by strongly basic resins, either as a complex vanadyl sulphate anion, or as a polyvanadate. The affinity for the resin is high, and the vanadium complex will displace uranium. Its absorption may be prevented, by reduction to the 4-valent state using SO_2, or alternatively, it may be recovered separately from the uranium, by allowing it to be absorbed, and then reducing to the 4-valent state by passing SO_2 solution through the resin. The vanadium is rapidly removed, leaving the uranium to be eluted in the normal way.

Molybdenum : Molybdenum, which occurs only rarely in leach liquors, is strongly absorbed, and accumulates on the resin during successive cycles. As it is not eluted by nitrate, but is readily removed by hydroxide, it is probable that it is absorbed from acid solution as a polymolybdate which has a high affinity for the resin, and is converted to molybdate, which has a low affinity, by the action of alkali.

In laboratory column experiments, an effect is sometimes formed which does not occur in industrial practice. It has been shown that the absorbed molybdenum, which is normally present in a band at the top of the column, is reduced to molybdenum blue by a photochemical reaction in the presence of uranium. The reaction, which does not occur in the absence of either light or uranium, appears similar to that previously observed in cellulose chromatography[16]. Molybdenum blue is almost impossible to remove from the resin; and laboratory tests with molybdenum-containing liquors should be carried out in shielded columns.

Thorium : Thorium forms an anionic sulphate complex, whose formula has not been established. It is absorbed by anion exchange resin, but the affinity is low, and it is easily displaced by uranium. Fig. 7 gives a typical curve of uranium and thorium absorption, from a solution containing 0.35 g/l U_3O_8 and 0.28 g/l ThO_2. At the final equilibrium point P, the U_3O_8 : ThO_2 ratio on the resin was 126 : 1. Complete elution of the trace of thorium present was readily achieved, using either nitrate or chloride solution.

Polythionates

Polythionate (SnO_6^{2-}, when n=2-6) can be formed in solution as a result of the partial oxidation of sulphide minerals in the ore during the leaching process. It is probable that thiosulphate is formed as an intermediate step, and that this process occurs more readily in alkaline than in acid solution[9]. As a result, difficulties due to polythionate are most common in the South African mines, where the ore is in con-

tact with an alkaline solution prior to the uranium process. In most other regions, the polythionate content of the liquors is low, even when sulphide minerals are present.

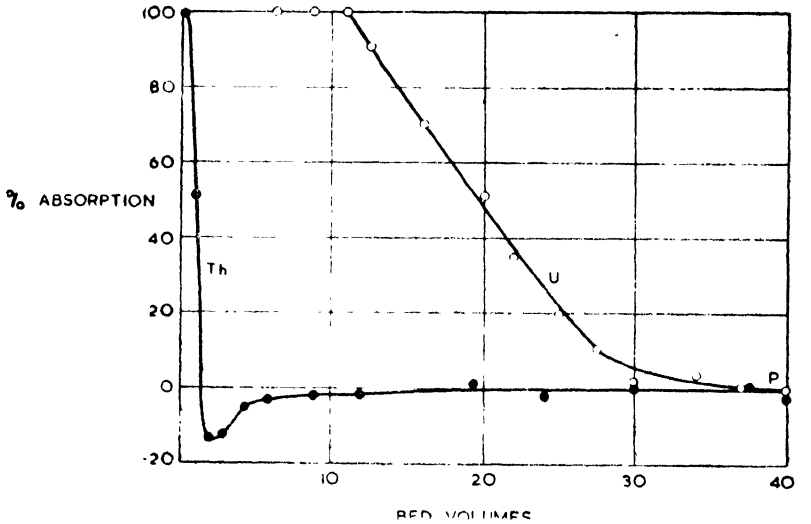

Figure 7.—Uranium and thorium absorption.

Fig. 8 shows the effect on the absorption of uranium from M|200 UO_2SO_4 solution, made by the presence of M|800 di, tri, and tetrathio-

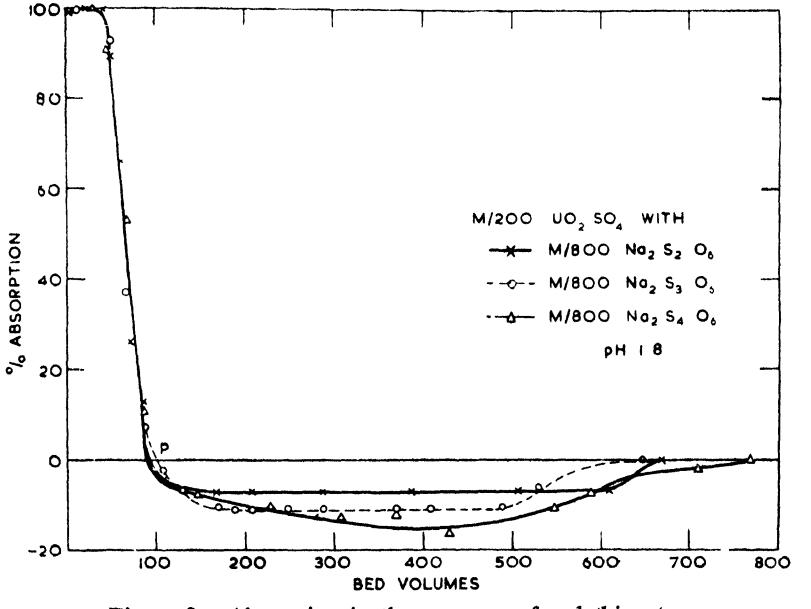

Figure 8.—Absorption in the presence of polythionates.

nate[17] . The affinities are considerably higher than that of the uranium complex, which is therefore displaced from the resin. At the final equilibrium points, the resin loadings are respectively 63, 7 and 3% of that obtained in the absence of polythionate. The uranium content of the resin is at its highest at point P ; if care is taken to ensure that the column is not run past this point, the loading is only slightly less than that given by a pure uranium solution.

Although the concentrations found in practice are rarely as high as those shown in Fig. 8, the effect can be cumulative, since the affinity of polythionate is so high that it is incompletely removed from the resin by the usual eluting solutions. The uranium loading therefore tends to fall with successive cycles. The accumulated polythionate can be removed by treatment with NaOH, to convert to thiosulphate and sulphate, followed by displacement of these ions by means of brine

$$2S_4O_6^{2-} + 6OH^- \leftrightharpoons 3S_2O_3^{2} + 2SO_3^{2-} + 3H_2O$$

When nitrate solutions are used for elution, the polythionates tend to be destroyed on the resin by oxidation, and the rate of poisoning is consequently reduced. One of the reaction products is elemental sulphur, which can cause blocking of the resin pores ; but there is evidence[9] that this element is removed by NaOH, probably after oxidation to thiosulphate.

Cyanide Complexes

Thiocyanate and the complex cyanides all have high affinities for strongly basic resins, and can cause difficulties due to displacement of uranium, and also by accumulation on the resin. The cobalticyanides and cobaltocyanides[9] have been shown to give the greatest difficulty, being so firmly held as to be virtually immovable. As a result, in South African uranium plants where traces of these ions occur, the useful life of the resin may be as little as 14 months ; and no completely satisfactory method of regeneration has been found. This problem occurs only in the Witwatersrand mines, where the ores are treated with cyanide for gold extraction before the uranium stage.

Metal Oxides

Leach liquors normally contain ferric iron and aluminium, frequently accompanied by phosphate. If the pH is raised above 2.0 ferric and aluminium phosphates, hydroxides, or basic sulphates tend to precipitate by hydrolysis. The passage of the liquors through unbuffered resin results in an increase in pH, by the removal of bisulphate from solution.

$$R_2SO_4 + H_2SO_4 \rightarrow 2RHSO_4$$

As a result of this process, the first entry of liquor into the column is frequently accompanied by precipitation of ferric salts in the resin bed. In laboratory tests, the deposit rapidly redissolves as more acid liquor

passes; but in large scale practice, the precipitate may partially block the bed, causing an uneven flow distribution which prevents complete re-dissolving. Deposits of ferric hydroxide and basic sulphate standing in contact with solution, slowly change to ferric oxide $Fe_2O_3.H_2O$, which is dissolved only with great difficulty in mineral acids[18]. Similar effects can occur with aluminium hydroxide, and as a result, oxides can slowly accumulate in the resin, blocking the pores and interfering with absorption.

This process is best prevented by acidifying all wash waters to pH2.0 by means of sulphuric acid, so as to maintain pH conditions in the bed permanently acid. The acid rinse following absorption elutes traces of uranium, and must be returned to the leach circuit to prevent loss.

Silica

Most leach liquors contain silica, in concentrations varying from 10-3000 ppm. In these acid solutions, free silicate ions are virtually absent, the silica being in the form of a sol which is normally unstable, and slowly deposits hydrated silica at a rate which increases with the original concentration. Since the colloid is negatively charged, it tends to be attracted to the positively charged quaternary groups on the resin surface, which consequently form sites for the initiation of deposition. As a result, a silica gel accumulates on the resin, blocking the pores. Resin beads which are contaminated in this way become white and opaque on drying. On calcination, they leave a spherical shell of silica, supported by a loose skeleton, showing that the bulk of the contamination is near the surface, although traces have penetrated to the centre of the beads.

The effect of silica poisoning is to reduce the exchange rate of the resin without significantly altering the total capacity. In a large scale life test, using De-Acidite FF, the resin was subjected to over 500 absorption and elution cycles, using a natural leach liquor, during a period of 2 years, without any clearing procedure. At the end of this time, the silica content had risen to over 5%; but the saturation uranium loading had decreased by only 6%. The rates of absorption and elution, however, were halved, and the daily output of uranium from the column was correspondingly reduced.

Although there is no means of completely preventing silica deposition on the resin, the effect is reduced to the minimum by the use of the acid rinse system. Freshly precipitated ferric and aluminium hydroxide tend to carry down silica by neutralisation of charge, and can thus increase silica poisoning unnecessarily.

Silica deposits, even of long standing, are easily removed from the resin by treatment with sodium hydroxide. The silicate thus formed is displaced from the resin by means of a neutral salt solution, after which the resin is treated with sulphuric acid to remove any metallic

hydroxides present. Fig. 9 shows the effect of NaOH concentration, and treatment time, on ash and silica reduction.

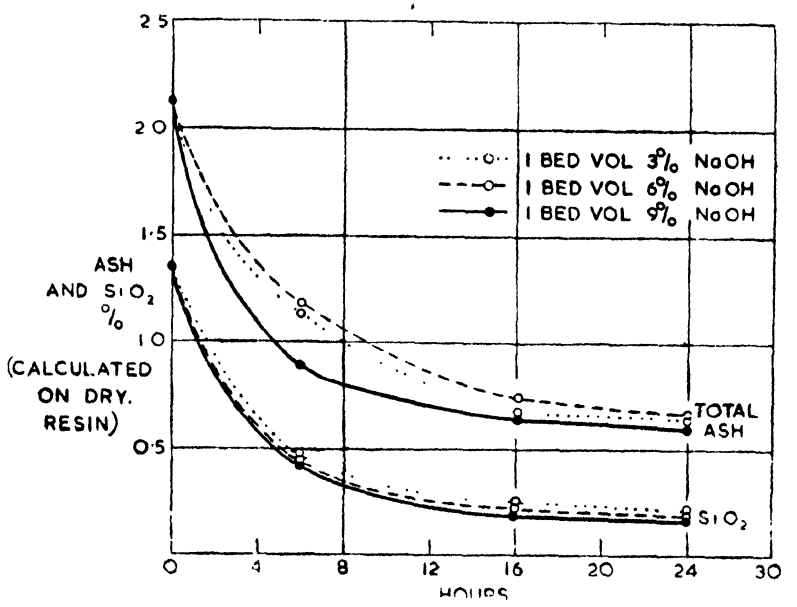

Figure 9.—Treatment of poisoned resin.

Organic Poisons

Organic flocculating agents are frequently added to the leached ore pulp to aid settling and filtration. The most common materials are polyhydroxy compounds, such as starch or Separan, and crude proteins such as glue. There is no evidence that the former have any influence on the ion exchange results; but proteins or their acid degradation products can become attached to the resin, if excessive quantities are added to the pulp.

The result is an organic fouling of the resin, which normally does not change the total uranium loading, but reduces the exchange rate, causing early breakthrough and slow elution. Similar effects have been observed when leaching floatation concentrates for which phenolic reagents have been used. In either case, the resin may be cleansed by treatment either with 4% caustic soda solution, or with 10% sodium chloride containing hypochlorite equivalent to 0.5% available chlorine.

Factors influencing Plant Design

Absorption Rate: Fig. 10a represents a typical column of resin, of infinite height, through which is passing a uranium-containing liquor. The concentration of uranium in the liquor at any point, as

a fraction of the input value, is plotted horizontally. In the resin RS, the solution is completely stripped of uranium, while the region OQ contains uranium-saturated resin in equilibrium with unchanged solution. The intermediate region QR is that in which absorption is occurring. For a given solution, the curve QR travels down the column at a fixed rate, and has a fixed length which determines the height of column required to treat the liquor. It is clear that the minimum absorption unit to give saturation of one column of resin, without loss of uranium, is a pair of equal columns PQ and QR in series. If the liner flow-rate is increased the gradient length Q'R increases, but to a lesser extent. Thus doubling the linear flow-rate, by halving the column area (Fig. 10b), increases the length QR by a factor of only 1.75, and the volume of resin used is consequently less than in case 6a. In large scale plant practice, the optimum bed depth is about 6 ft., which is sufficient to give good absorption characteristics and is not so deep as to cause difficulty in backwashing. In calculating the plant size required for a particular solution, the linear flow-rate required to give a gradient length Q'R of 6 ft. is determined in laboratory experiments. The diameter of the full scale plant is then calculated, from the total flow to be treated. The normal flow rate used for 2 column absorption is about 6 column volumes per hour (retention time 4 minutes per column, based on 40% voids) although the correct rates must be determined separately for each solution.

In laboratory practice, using tall narrow columns, it is possible to reduce the retention time considerably below the ideal figure, without seriously reducing the loading or purity of product. The effects of such increases in flow rate are shown in Table 2.

TABLE 2

Retention Time (min)	Inter-column Analysis % of head	Resin Loading g/l U_3O_8	Product Purity % U_3O_8
8	98	76.7	96.1
6	96	76.3	95.0
4	93	75.5	95.5
2	86	71.1	93.5
1	79	65.1	90.1

It is not possible to take full advantage of this effect in industrial practice, since in the large-diameter columns used, the chromatographic boundaries are necessarily less sharp.

The overall size of the ion exchange plant can be reduced by determining experimentally the flow rate at which the concentration gradient QR is approximately 12 ft. in length. This rate is more than double that required for a 6 ft. gradient length, and the column area is correspondingly reduced. By using 3 columns in series (Fig. 10c), the absorption gradient is contained in 2 of them while the third is saturated. Accordingly, the complete ion exchange unit represented

by Fig. 10b consists of 3 columns, one of which is used for elution while the unit represented in Fig. 8c consists of 4 columns of slightly less than half the size, representing an overall reduction in the plant size. The 4 column units are used particularly in those cases where the $Fe^{+++}|UO_2^{++}$ ratio in solution is high, giving slow iron|uranium exchange rates.

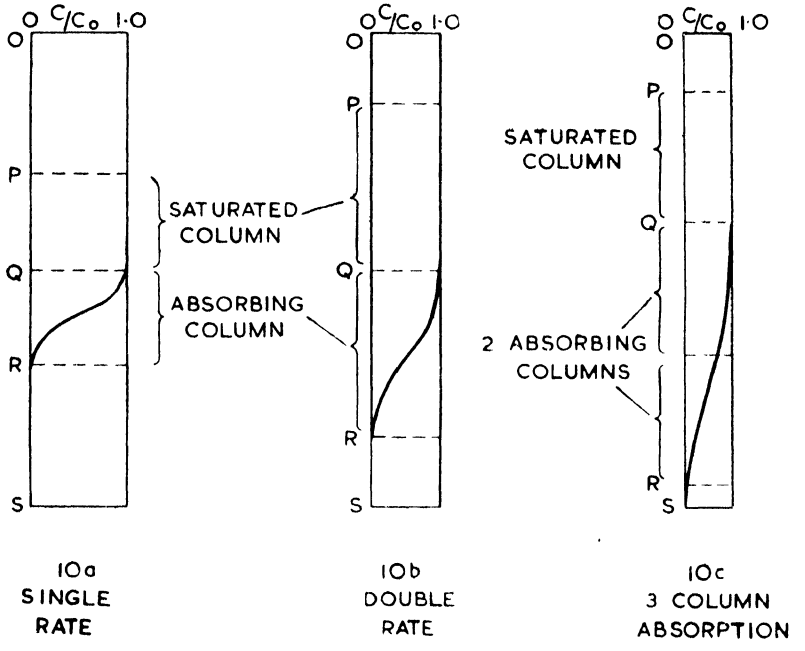

Figure 10.— Effect of flowrate.

Elution Rate : The rate of elution of uranium from a resin by means of a concentrated solution of another ion, at a constant flow rate is controlled by the diffusion rate of the complex, which is a constant. The quantity of uranium emerging at any time t, and hence at any volume v, is proportional to the quantity remaining on the resin. Then :——

$$-\frac{dc}{dv} = K.\ Cv$$

When Cv = the concentration of residual uranium after the passage of volume v. Then if f is the percentage eluted by a column v,

$$\frac{f}{100} = 1 - \frac{Cv}{Co}$$

$$= 1 - e^{-Kv}$$

Thus a plot of (1 — f|100) against v should give a straight line, of slope K. This is found to be true in practice, provided that the range of resin particle size is small. This value of K decreases with increasing particle size, so that with a wide size distribution, the smaller beads are eluted first; and the measured value of K decreases throughout the process.

Fig. 11 gives the results obtained in elution tests using 100ml columns of De-Acidite FF in conjunction with Molar nitrate, and Molar chloride-

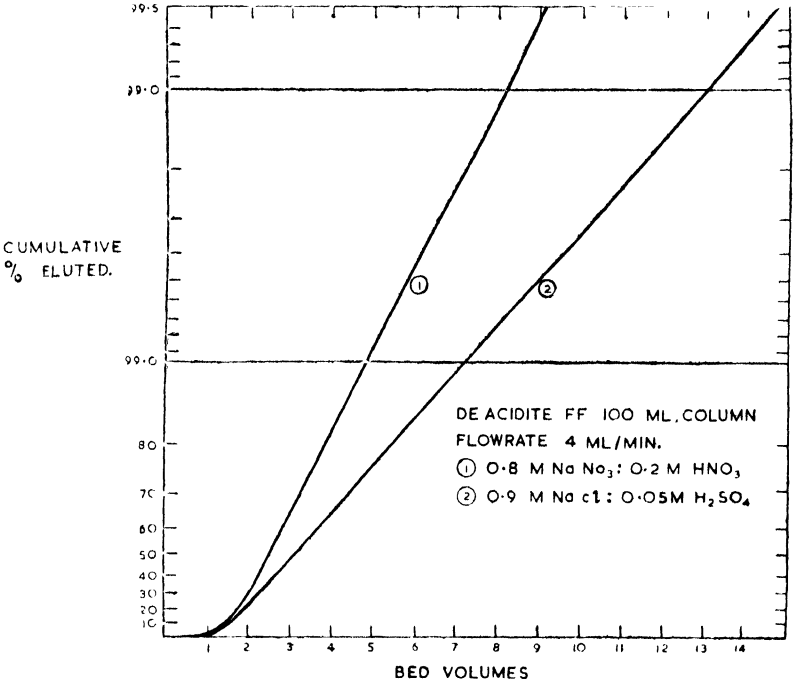

Figure 11.—Elution rate.

sulphate eluent, at a 10 minute retention time. The former is considerably more efficient, but the chloride-sulphate mixture is frequently used on account of its lower cost.

If the elution process were purely particle-diffusion controlled, the volume of eluent required would be inversely proportional to the flow rate, giving a constant elution time. Fig. 12 gives the results of tests on the elution of a sample of De-Acidite FF, having a capacity of 1480 meq|l and water regain of 0.80, with a solution containing 1.0M NaCl, 0. 2M $MgSO_4$ and 0.05M H_2SO_4. With increasing flow-rate, the total time of elution decreases, although the volume of eluent required increases. It follows that the rate of elution process is partially controlled by a film-diffusion mechanism. In industrial practice, a compromise must be made between elution quantity and time.

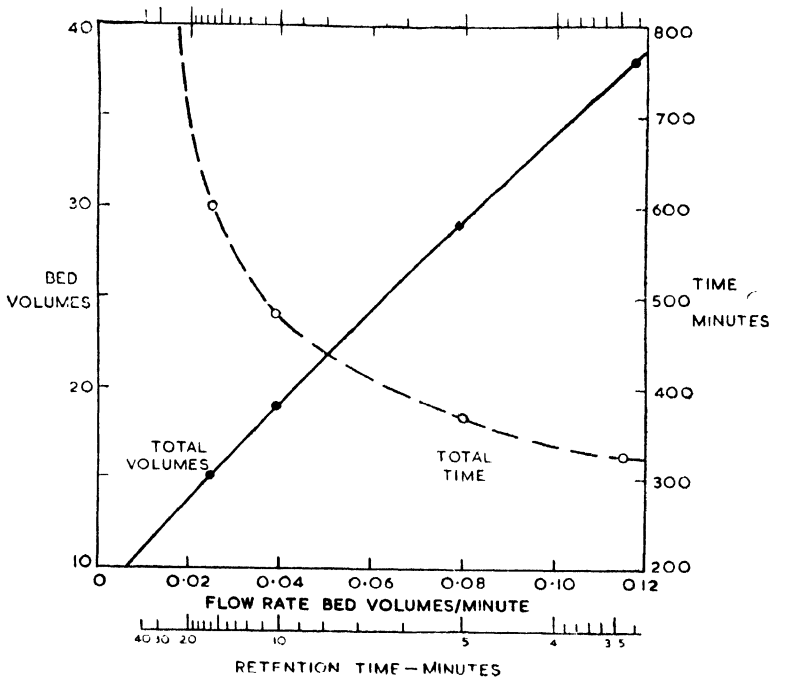

Figure 12.—Elution volume and time.

The Balance of absorption and elution times : In the calculation of plant size from absorption data, the first object is to adjust the pregnant liquor flowrate so as to give the shortest cycle time compatible with full resin loading, subject to the limitation that the absorption time must be sufficient to allow time for backwash and elution of the remaining column.

In the case of very low grade liquors, this limitation presents no problem. For example, in the hypothetical case of a pregnant liquor containing 0.1 g/l U_3O_8, and giving a saturation loading of 50 g/l U_3O_8, with a contact time of 4 minutes, the absorption time is $\frac{50 \times 4}{0.2 \times 0.4}$ minutes, that is 42 hours. This is greatly in excess of the maximum time required for elution; and consequently, long eluant contact times can be allowed, in order to reduce the eluant quantity to the minimum. In this case, experimental work would be directed towards reducing absorption time by means of higher flowrates, if necessary with a reduction in resin loading.

In the opposite case of relatively rich liquors, particularly those of low Fe^{+++} content, the optimum plant size calculated from absorption data may present an insoluble elution problem. A liquor containing

3.0 g/l U_3O_8, and requiring a minimum contact time of 4 minutes to give a saturation loading of 80 g/l U_3O_8, has an absorption time of $\frac{80 \times 4}{3 \times 0.4}$ minutes, or 4.6 hours. As this is less than the minimum time required for backwash and elution, advantage cannot be taken of the rapid absorption characteristics of this liquor, and it is necessary to increase the plant size above the optimum value, in order to provide sufficient time for elution. Alternatively, very high elution flowrates may be used to reduce elution time to the minimum, even though these rates inevitably involve the use of large quantities of eluant. The balance which must be struck between these two undesirable operations can only be decided by experiment in individual cases.

The difficulty can be greatly reduced by the use of a four column unit, in which two columns are eluted simultaneously, either in series or in parallel. The effective elution time is then reduced by half, although the wash time remains unchanged.

Moving Resin Plants : At the Consolidated Denison Mine, in the Blind River area of Ontario, Canada, the first of a new type of uranium plant has recently commenced service on a large scale[19]. In this unit, the three operations of absorption, backwash and elution are carried out in three separate units, each one of which can thus be designed to give the optimum conditions for its own operation. The absorption unit consists of a series of resin columns, through which liquor passes continuously. As the first in line becomes saturated, the resin is transferred to the backwash vessel, after which the absorption vessel is filled with new resin, and returns to service as the last on line. The fully loaded resin after backwashing is transferred into the last of a series of columns through which eluting solution is passing, while simultaneously, fully eluted and washed resin in the first elution column is returned to the absorption system. A countercurrent elution process is thus obtained, and it is possible to achieve a high elution rate, together with a small volume of concentrated eluate. In addition, the flexibility inherent in the moving bed process reduces considerably the problem of balancing absorption and elution times. A general view of the ion exchange unit at the Consolidated Denison Mine is given in Fig. 13.

Resin-in-Pulp Process : The ion exchange column process of necessity requires clear liquors; and on the industrial scale, this can result in a heavy capital expenditure on acid-proof filters or thickeners, in the case of ores which have poor settling and filtration properties. In the resin-in-pulp processes, the resin is contacted directly with the leached ore pulp, and then separated for elution. A number of different resin-in-pulp techniques have been described; but so far only one, the American basket process[5, 20] has been operated on an industrial scale. The ore pulp, after leaching, is completely desanded using rake classifiers and cyclones, the slimes fraction, at about 5-8% solids, being passed

through a series of large launders, in each of which stainless steel baskets containing the resin are agitated vertically. The basket process is thus effectively a series of separate equilibrations, and six to eight separate stages, each with a contact time of about 10 minutes, are required for complete absorption of uranium. When the resin at the head of the line is fully loaded, the flow of pulp is diverted from it, and the launder is emptied. The resin is then washed, and by changing the liquid flows this unit becomes the last of a series of 4-6 undergoing elution.

The basket R.I.P. process has proved of particular value in plants, such as the Moab Mill, Utah, U.S.A.[20], which treat a variety of different ores, with widely varying properties. It has not, however, given the capital savings originally expected since the basket plant is much larger than a column plant of the same output. In recent years, the efficiency of countercurrent decantation for the washing and de-watering of ore pulps has been greatly increased by the use of cyclone de-sanding, and of flocculating agents such as Separan which have enabled thickener sizes to be greatly reduced. As a result, there is now less necessity for the R.I.P. process, and all the new plants constructed in 1957 have been based on column operation. Nevertheless, the subject is still under active study in many laboratories.

The A.E.C. Higgins contactor[21] uses a continuous cylic system consisting of two vertical legs joined top and bottom. A double-acting ram, synchronised with a valve system, raises the resin in one leg on one stroke, and forces down the other on the reverse stroke. The upflow resin leg is divided into two by a valve, the resin being eluted by a downflow stream in the lower section, while the pregnant pulp flows down through it in the upper section. Pilot scale units have been operated successfully, and larger installations are contemplated.

A recent paper[22] has described a new type of contactor, containing no moving parts. The resin and pulp are mixed in a central chamber of the contactor, after which they overflow into a separating chamber, from which they are removed in separate streams. Each contactor forms one equilibration stage, and a series of eight is used in countercurrent flow for absorption, with a similar group for elution.

These processes appear to have a number of advantages over the basket technique, including smaller size and greater contacting efficiency; but they suffer from the same disadvantage of requiring a low pulp density. The Weiss-Swinton jigged-bed process[23], developed at C.S.I.R.O. Melbourne, Australia, overcomes this difficulty by using absorption columns in which the resin is retained by top and bottom screens, and is maintained in a fluidised state by applying a vertical pulsation to the pulp, which passes upflow through the resin. Using large-bead resin, with a completely desanded pulp, it is possible to operate with pulps containing 25-40% solids. The Weiss-Swinton process has been suc-

cessfully operated for long periods on the pilot plant scale, and larger scale operations are envisaged.

The necessity for desanding has been eliminated in a new technique, the membrane-in-pulp process, recently demonstrated at the Chemical Research Laboratory, Teddington, England[24]. Permaplex A-10 anion exchange membranes are held in frames in launders, through which the leach pulp passes at 60-70% solids, maintained in suspension by air agitation. The general flowsheet is similar to that of the basket process, but the absence of moving parts and the possibility of dispensing with the desanding stage gives the membrane process a considerable potential advantage. It has so far been demonstrated only on a large laboratory scale, and some time must elapse before the potentialities of the process can be fully evaluated.

Acknowledgement

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TREATMENT OF MONAZITE SANDS WITH SPECIAL REFERENCE TO INDIAN PRACTICE

*By H. N. Sethna & S. Fareeduddin**

Monazite, which is essentially a phosphate of cerium earths, is one of the major sources of thorium. Before the advent of nuclear energy, the main use of thorium was in the manufacture of gas mantles; but now as it is known that thorium (Th^{232}) undergoes conversion under neutron bombardment to U^{233} which can be used as a nuclear fuel, the importance of thorium has increased considerably.

Monazite deposits are found mainly in India (Kerala) and Brazil Other deposits of monazite and thorium bearing minerals are found in South Africa, Madagascar, Florida (USA), Australia, Ceylon and Canada. The Indian deposits are particularly well known for their high thorium content and vastness. Recently the Department of Atomic Energy, Government of India, has announced a new occurrence of these deposits in the north eastern part of India, which are expected to be as vast and of the same quality as the Kerala (previously Travancore) deposits. Approximate compositions of typical monazite concentrates analysed are shown in Table I.

TABLE I.

Constituent	Indian(6)	Brazilian (1)	U. S.(1)*	South African (2) (Monazite rock)	Madagascar (3)
ThO_2	8.88	6.5	3.1	5.9	8.75
U_3O_8	0.35	0.17	0.47	0.12	0 41
$(RE)_2O_3$	59.37**	59.2**	40.7**	46.41**	46.2**
Ce_2O_3	28.46	26.8	—	24.9	23.2
P_2O_5	27.03	26.0	19.3	27.0	20.0
Fe_2O_3	0.32	0.51	4.47	4.5	—
TiO_2	0.36	1 75	—	0.42	2.2
SiO_2	1.00	2.2	8.3	3.3	6.7

* Florida sand containing about 70% monazite.
** Includes Ce_2O_3.

The conventional process for recovering rare earths and thorium from monazite consisted of digestion of the sand with concentrated sulphuric acid followed by the dissolution of the digested products in water. In this process the sand is satisfactorily decomposed without any fine grinding but the solution contains all the phosphates thereby seriously complicating the subsequent separation and purification of

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thorium and rare earths. This disadvantage could be overcome if the thorium in solution is separated by solvent extraction. We believe that some amines have shown good selectivity for thorium(4) and in the future this may be one of the methods that could be adopted for its recovery.

The Indian Rare Earths Factory at Alwaye uses a caustic soda treatment for the decomposition of monazite sands and the process consists of the following main stages. (See figure 1).

(1) Reaction of finely ground monazite sand with hot concentrated aqueous caustic soda solution, which converts the rarte earths and thorium into their respective hydroxides and the phosphate into trisodium phosphate.

(2) Separation of the insoluble hydroxide from the dissolved phosphate and excess caustic soda.

(3) Recovery of the trisodium phosphate.

(4) Separation of rare earths from thorium by leaching with hydrochloric acid.

Further purification of thorium and its conversion to either a sulphate or a nitrate is carried out at the Atomic Energy Establishment factory at Trombay near Bombay.

We consider that this process has several advantages over the conventional acid process :—

(1) The phosphate present is eliminated as an useful by-product which facilitates the subsequent recovery and purification of thorium and rare earths.

(2) The process uses chemicals most of which are produced in India.

(3) The products obtained are sufficiently pure to be suitable for most commercial uses without further purification.

Reaction of monazite with caustic soda

The monazite sand as received is fed to a ball mill where it is ground to finer than 300-mesh in a closed circuit system using an air classifier.

The ground sand in batches of ½ a ton is intimately mixed in a mixer with 50% caustic soda solution and the resulting mass fed to a conical mild-steel tank and heated to approximately 150°C with the addition of fresh caustic soda to give a monazite sand caustic soda

ratio of about 1 : 1. The final concentration of caustic soda is about 65 to 70%.

The mixture is agitated during the reaction which lasts for about 3 to 4 hours. Most of the monazite is decomposed in this period.

Separation of hydroxide cake from trisodium phosphate and sodium hydroxide

The hydroxides—trisodium phosphate mixture is dumped in a tank containing dilute wash liquors from a previous decantation and the slurry is heated to approximately 90°C and the density adjusted to about 30° Be. The slurry is allowed to settle for about 12 hours when the supernatant liquid containing most of the trisodium phosphate and the excess caustic soda is drawn off and sent to the trisodium phosphate recovery section. The hydroxides are washed once again with hot water, allowed to decant and the supernatant liquid drawn off to be re-used for a subsequent extraction of trisodium phosphate.

By this means the free alkalinity in the hydroxides is reduced from about 70 gms. per litre (expressed as free NaOH) to about 15 gms. per litre. The mixture of hydroxides is then fed to a vacuum leaf filter and washed to reduce the alkalinity before being treated for the separation of rare earths from thorium.

Recovery of trisodium phosphate

The solution from the decantation tanks is filtered and fed to a vacuum crystallizer. In the crystallizer the solution of trisodium phosphate and caustic soda is cooled from about 70°C to 20°C in two stages at which temperature most of the trisodium phosphate crystalizes out. The mixture of trisodium phosphate crystals and dilute caustic soda solution is fed to a continuous centrifuge and the centrifuged trisodium phosphate is dried in a hot air conveyor drier. The dry trisodium phosphate contains approximately 19% P_2O_5, and is purer than trisodium phosphate manufactured by the usual process of neutralization of phosphoric acid.

Separation of rare earths from thorium

The washed hydroxide cake is treated in a rubberlined tank with 21 to 22° Be. hydrochloric acid. Sufficient quantity of hydrochloric acid is added to dissolve only the rare earths whilst the thorium remains undissolved. Iron is precipitated by oxidising it to the ferric stage and suitable precautions are taken to prevent oxidation of cerium to the ceric stage. The pH of this slurry is in the neighbourhood of 3. The slurry is pumped to a plate and frame type filter press using rubberlined equipment.

The filtrate, after removal of lead, is converted to the fused mixed

rare earths chloride by heating it in an enamelled cast iron vessel to a boiling point of approximately 145°C and then pouring into steel drums where it solidifies on cooling.

The thorium hydroxide is washed and the wash waters are converted either to the mixed rare earths carbonate by the addition of sodium carbonate or to the mixed rare earths hydroxide by the addition of caustic soda. Both these rare earth compounds are dried in a rotary drier before being packed in steel drums.

The cake contains all the thorium present in the monazite and most of the uranium. It also contains a certain percentage of rare earths and other insoluble impurities.

Purification of thorium

The crude thorium hydroxide cake is dissolved in an excess of hydrochloric acid and the resulting chloride solution is filtered on a plate and frame type filter press to remove insoluble impurities like ilmenite, zircon, etc. The clear filtrate is treated with an excess of 50% sulphuric acid. Most of the thorium is precipitated as a sulphate whilst most of the rare earths and most of the uranium remain in solution. The thorium sulphate is centrifuged in a rubberlined centrifuge and the solution is sent for recovery of thorium, rare earths and uranium which are in solution. This sulphate is not pure enough and is further purified by reprecipitating with 50% sulphuric acid to give a purer thorium sulphate.

The pure thorium sulphate is converted to the hydroxide by reacting it with ammonium hydroxide. This is filtered and washed on filter presses with distilled water to remove all the water soluble impurities. The thorium—hydroxide is then dissolved in chemically pure nitric acid to give a solution of thorium nitrate which is filtered and evaporated to the required strength of thorium nitrate in a glass lined evaporator. The molten nitrate is allowed to solidify in aluminium dishes and then packed in glass bottles or lined steel drums.

The solution obtained from the precipitation of thorium sulphate is treated for the recovery of thorium, rare earths and uranium by fractional precipitation with hydrofluoric acid.

The rare earths and thorium fluoride re-enter the process after treatment with caustic soda whilst the uranium fluoride is converted to sodium—uranate for subsequent purification by solvent extraction.

In order to avoid the use of large quantities of chemicals and to obtain a purer material, experiments are being carried out on a laboratory and pilot scale (5) on the following lines. The crude thorium and uranium cake is dissolved in hydrochloric acid and the solution is treated with oxalic acid to precipitate thorium and a part

of the rare earths as oxalates. The oxalate after washing is converted to hydroxide by treating it with caustic soda. The filtrate containing sodium oxalate is recycled with some make-up oxalic acid to the first stage and the hydroxide cake after washing is dissolved in nitric acid. The clear solution is extracted by tributyl phosphate to obtain pure thorium nitrate as indicated by Audsley, A, and Coworkers (2).

Data obtained so far indicate that recycling of the filtrate containing sodium oxalate is feasible and the recovery of thorium and volumes of liquors handled are quite comparable with the present process. Modifications in the existing plant at Trombay will be carried out after these investigations are finalised.

Manufacture of nuclear pure uranium metal

A uranium metal plant is under construction at Trombay for producing nuclear pure uranium metal. This plant is expected to go into operation by the middle of 1958.

The raw material for this plant will be sodium uranate obtained from the processing of monazite and other ores. Processing of monazite sand as employed in India gives uranium in the form of uranium tetrafluoride. Uranium tetrafluoride will be reacted with sodium carbonate and hydrogen peroxide to dissolve the uranium and remove most of the impurities. The dissolved uranium will then be precipitated by sodium hydroxide. The diuranate will then be dissolved in nitric acid and filtered. The filtered solution after adjustment of acidity (2N HNO_3) will be extracted in a pulsed packed column by a mixture of tributyl phosphate and kerosene (See figure 2). The extract will be scrubbed by dilute nitric acid to remove impurities such as thorium, rare earths, iron, etc. The organic extract will be stripped with water to obtain a pure uranyl nitrate solution. Pilot plant experiments have shown that the purity of this uranyl nitrate is suitable for use in nuclear reactors. The aqueous uranyl nitrate solution is then treated with amonia to obtain ammonium diuranate, which is converted to the trioxide and reduced to the dioxide. The fluoride will be prepared by the dry method using gaseous hydrogen fluoride at about 400°C. Calcium will be used for reduction of the fluoride to metal.

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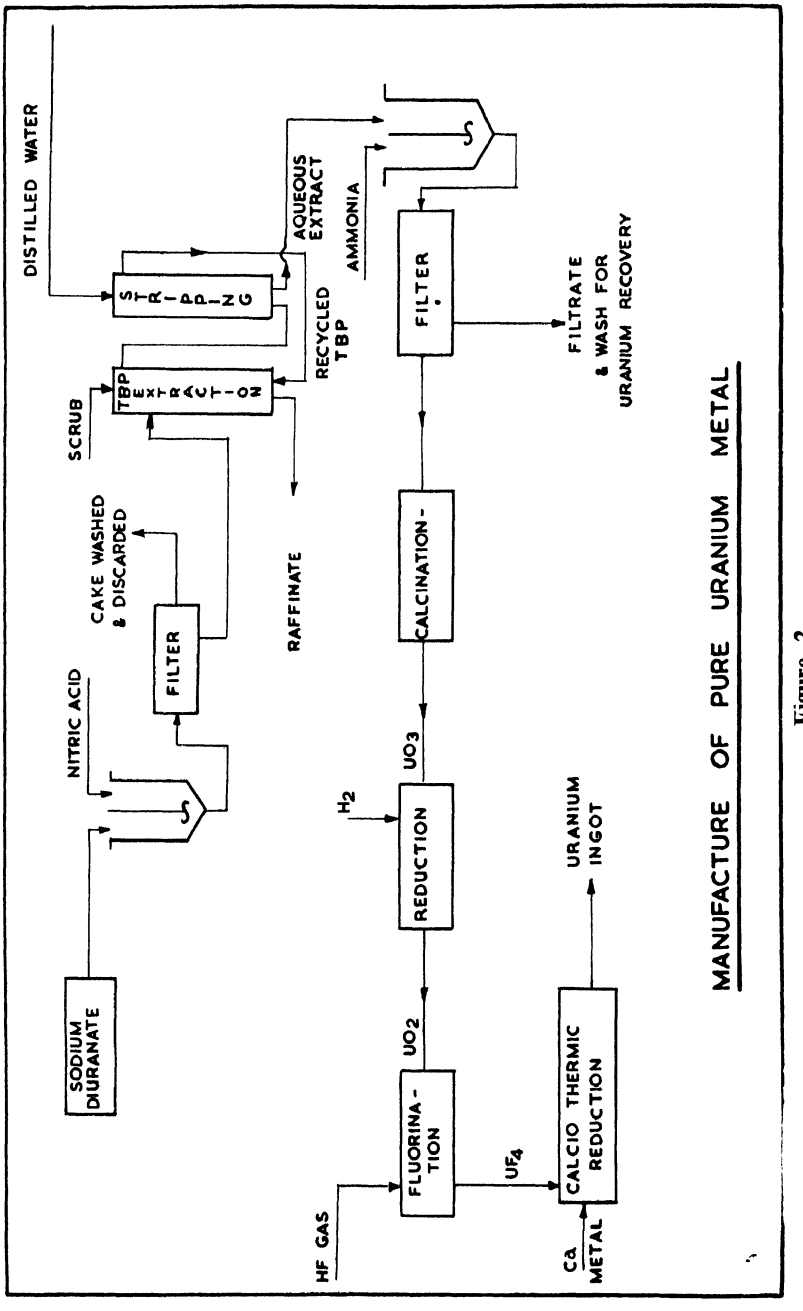
MANUFACTURE OF PURE URANIUM METAL
DISTILLED WATER
STRIPPING
AQUEOUS EXTRACT
AMMONIA
FILTER
FILTRATE & WASH FOR URANIUM RECOVERY
TBP EXTRACTION
SCRUB
RECYCLED TBP
RAFFINATE
CAKE WASHED & DISCARDED
FILTER
NITRIC ACID
SODIUM DIURANATE
CALCINATION
UO_3
H_2
REDUCTION
UO_2
FLUORINATION
UF_4
HF GAS
CALCIO THERMIC REDUCTION
Ca METAL
URANIUM INGOT

Figure 2.

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APPENDIX

Analysis of the products manufactured at Alwaye and the thorium compounds manufactured at Bombay are given below :—

(1) *Trisodium Phosphate—Crystalline* :

P_2O_5	...	18 — 20 %
NaOH	...	1 — 2.6%
Na_2CO_3	...	0.2 — 0.5%

(2) *Rare Earth Chlorides* :

(i) Ceric Oxide (CeO_2)	...	21.5	—	22.0 %
(ii) Lanthanum Oxide (La_2O_3)	...	9.0	—	9.1 %
(iii) Neodymium Oxide (Nd_2O_3)		8.3	—	8.5 %
(iv) Praesodymium Oxide (Pr_2O_3)		2.6	—	2.7 %
(v) Samarium Oxide (Sm_2O_3)	...	3.2	—	3.3 %
(vi) Yttrium and other Yttrium group R.E. Oxides (Y_2O_3)	...	0.5	—	0.53 %
(vii) Total Oxides (Total of i to vi)		45.0	—	47.0 %

Impurities :

(i) Calcium Oxide CaO	...	0.8	—	1.0 %
(ii) Sodium Oxide (Na_2O)	..	1.08	—	1.2 %
(iii) Iron as Fe	...	0.002	—	0.005%
(iv) Lead as Pb	...	0.1	—	0.15 %

(3) *Rare Earth Carbonates* :

(i) Ceric Oxide (CeO_2)	...	32.5	—	33.0 %
(ii) Lanthanum Oxide (La_2O_3)	..	13.4	—	13.5 %
(iii) Neodymium Oxide (Nd_2O_3)	.	12.6	—	12.7 %
(iv) Praesodymium Oxide (Pr_2O_3)		3.9	—	4.0 %
(v) Samarium Oxide (Sm_2O_3)	...	4.9	—	4.95 %
(vi) Yttrium and other Yttrium group R.E. Oxides (Y_2O_3)	...	0.7	—	0.75 %
(vii) Total Oxides (Total of i to vi)		68.0	—	70.0 %

Impurities :

(i) Calcium Oxide (CaO)	...	0.06	—	0.08 %
(ii) Sodium Oxide (Na_2O)	...	0.08	—	0.10 %
(iii) Chlorides	...	Traces		
(iv) Iron as Fe	...	0.08	—	0.10 %

(4) *Dried Crude Thorium Hydroxide* :

(i) Total Oxides	...	55	—	65 %
(ii) Thorium Oxide ThO_2	...	45	—	55 %
(iii) Thorium Oxide/Total Oxide	...	80	—	90 %
(iv) % P_2O_5/ThO_2	...	Max.		3.0 %

(5) *Thorium Sulphate I* :

(i) Total Oxides	...	42.0	—	44.0 %
(ii) Thorium Oxide ThO_2	...	41.6	—	43.6 %
(iii) Thorium Oxide/Total Oxide	...	99.0	—	99.50 %
(iv) P_2O_5	...	<0.1 %		

(6) *Thorium Nitrate* :

(i) Insolubles in water	...	Nil
(ii) Total Oxides	...	48%
(iii) ThO_2/Total Oxides	...	>99.99 %
(iv) P_2O_5	...	<0.002%
(v) Fe	...	<0.001%
(vi) SO_4	...	<0.5 %

Discussions

Mr. N. S. K. Prasad : In the reduction of UF_4, has calcium any special advantage over magnesium, the latter being cheaper material?

Due to the difficulty in the handling of anhydrous HF, would it not be advantageous to use NH_4HF_2 or fluocarbons, such as freons, which are being used in other countries in the preparation of UF_4. In Italy a plant using Freon-12 is said to be in operation and the process is claimed to be competitive with others.

Author's Reply : With magnesium, a much purer UF_4 is required. For instance, the UF_4 must be extremely dry and should contain no oxygen. I would not like to take a risk and therefore initially we will use calcium.

There are no abnormal difficulties in handling HF. HF is cheaper than the fluorine compounds mentioned; hence it is preferable to use HF. I do not think that any other fluorine compound could compete with HF.

Mr. P. P. Bhatnagar, (*National Metallurgical Laboratory, Jamshedpur*) : The calcium for the reduction of UF_4 has to be evidently distilled, free from N_2. Would it not be more expensive to use Ca than Mg? Are there any plans for producing distilled calcium?

Author's Reply : Possibly it would be cheaper to use Mg, but there are certain difficulties when using it, as explained before.

Initially it will be imported, but if consumption demands, we may go in for a small CaO reduction plant.

Dr. A. B. Chatterji, (*National Metallurgical Laboratory, Jamshedpur*) : The use of Mg or Ca as a reductant would depend on the ultimate impurities which can be tolerated in U-metal. I feel that with Ca the reduction will proceed further than with Mg as CaF_2 has higher free energy of formation than MgF_2, with the result that Ca reduction will yield purer uranium.

Author's Reply : No comments.

Mr. V. V. Dadape : Could we not replace the solvent extraction step for purification by chemical precipitation.

Author's Reply : We feel that by any precipitation techniques the impurities removed will not be to the same extent as by solvent extraction.

BRAZILIAN PRACTICE FOR MONAZITE TREATMENT

By P. Krumholz *

Coastal deposits of monazite sand have been exploited in Brazil since the end of the 19th century. Those deposits, extending from the northern border of the State of Rio de Janeiro, over the State of Espirito Santo to the State of Bahia, were in part so rich in monazite, that their exploitation was possible and actually performed, using very primitive technical resources. With the gradual exhaustion of the richest deposits, which represented only a small fraction of the total Brazilian occurrences, sands poorer in monazite and of a more complex composition had to be treated. A systematic exploitation of low grade deposits started, however, only in the last ten years.

The crude sand contains around 10% of heavy minerals, of which monazite represents a fraction between 10 and 15%. First the heavy minerals are separated from the bulk of the silica on a battery of Humphrey spirals. Then ilmenite and rutile are removed by means of electrostatic separators and finally the monazite separated from zircon on high capacity magnetic roll separators. A concentrate containing about 90% of monazite is so obtained with a recovery of about 80%. Final purification to about 98% is achieved by means of highly selective rotating disc magnetic separators.

The monazite so obtained contains about 64% of rare earths oxides, 5.5 to 6% of thorium oxide and 0.15 to 0.2% of uranium oxide. Table 1 gives the relative composition of the rare earths.

Table 1.—Relative composition of rare earths from Brazilian monazite.

CeO_2	47 %	Dy_2O_3	0.35 %
La_2O_3	24 %	Ho_2O_3	0.035%
Pr_6O_{11}	4.5 %	Er_2O_3	0.07 %
Nd_2O_3	18.5 %	Tm_2O_3	0.005%
Sm_2O_3	3 %	Yb_2O_3	0.02 %
Eu_2O_3	0.055%	Lu_2O_3	not determined
Gd_2O_3	1 %	Y_2O_3	1.4 %
Tb_4O_7	0.1 %		

Until 1948 all monazite mined in Brazil had been destined for export. During that year, the operation of the first industrial unit for the chemical processing of monazite was started, encouraged by the Brazilian Government. The unit, later increased to a production capacity of 3,000 tons of monazite per year, uses the alkali process for the opening up of monazite. A second, smaller installation, put in operation later, uses the conventional sulphuric acid process. The following discussion refers to the practice of the first installation.

* Research Laboratory of Orquima S. A., Sao Paul, Brazil.

It has been known since long, that monazite can be attacked by alkalies and methods have been proposed for a technical application of this process[1]. The alkali process has, however, never found a practical application until it has been revived and perfected recently in France[2]. The process in use in Brazil at present is based on the French process. Several years of experience with a large scale operation have led to many modifications and improvements.

Monazite is ground in steel ball mills to 99% minus 300 mesh. The attack with caustic sode solution is performed, contrary to the original practice, in closed vessels at a temperature around 170° and a pressure of several atmospheres. This results in a very clean and easily controllable operation. The autoclaves, built from nickel clad steel, are provided with a steam jacket and a heavy, anchor type agitator and hold 1250 kg. of monazite per charge. Caustic soda is used in an excess of about 100% over the theoretically necessary amount. The product of the reaction is diluted with water and the hydroxides of the rare earths and of thorium separated from the trisodium phosphate and the excess of caustic soda, present in the solution by filtration through iron filter presses. The cake is washed with water until phosphates are absent. Trisodium phosphate is recovered from the original filtrate by crystallization in a battery of Swenson- Walker type crystallisers cooled to 15° and final centrifugation. The mother liquor, containing the excess of caustic soda and some phosphate is concentrated to about 400 g NaOH per liter in a double effect vacuum evaporator. About 50% of the recovered caustic soda is recycled into the process. A complete recirculation is not advisable, as soluble impurities, particularly silicates, accumulate in the liquor and seriously affect the filtrability of the hydroxides.

Separation of the rare earths from thorium follows the French practice if rare earths chlorides are the desired final product. The mixture is suspended in water and the rare earths solubilised preferentially at 70°, by additional of hydrochloric acid until a final pH of 3.5 to 4. The thorium hydroxide is separated from the solution of the rare earths chlorides by filtration in wooden filter presses. This solution contains about 300 g of rare earth oxides per liter and is practically free of thorium and of phosphates. It is finally evaporated in cast iron pans to a content of 45|46% of rare earths oxides.

A typical composition of the crude thorium hydroxide is given in Table 2.

Table 2—Composition of crude thorium hydroxide obtained from mixed rare earths and thorium oxides by leaching with hydrochloric acid.

Acid insoluble	20%	Fe_2O_3	Al_2O_3	3%
ThO_2	60%	P_2O_5		2%
Rare Earths oxides	4%	SiO_2		2%
UO_3	2%	Cl		5%

If the rare earths are to be obtained in the form of sulfates or of double sulfates, the original process must be modified essentially[3]. It is no longer possible to obtain a satisfactory separation of thorium and rare earths by selective leaching. The mixture of the hydroxides is dissolved completely in sulphuric acid, not exceeding a temperature of 45° and a concentration of 80 g total oxides per liter. Thorium hydroxide is precipitated thereafter by addition of diluted ammonia until a final pH of 6. Contrary to the behaviour of chloride solutions where thorium hydroxide precipitates quantitatively at a pH of 4, complete precipitation of sulfate solutions requires a pH of about 6, probably due to a sulfate complexing of the thorium. Due to the high final pH and the presence of sulfate, the thorium precipitate contains considerable amounts of rare earths. The latter can be solubilised by prolonged washing of the precipitate with water or better by leaching with diluted hydrochloric acid. Finally, a thorium hydroxide results, containing about 10% of rare earths on the ThO_2 content, the other impurities being essentially the same as in the cake originating from a leaching with hydrochloric acid.

The rare earths contained in the filtrate from the thorium hydroxide are recovered in the form of double sodium and rare earths sulphates by slow addition of anhydrous sodium sulfate. By carefully adjusting the quantity of the sodium sulfate used, it is possible to retain in solution most of the yttrium and the heavy earths as well as about 50 to 60% of the gadolinium contained in the original material. Those elements are then recovered from the filtrate of the double sulfates by precipitating carbonates from the boiling solution.

The crude thorium hydroxide, resulting from either the hydrochloric or the sulphuric acid operation is optionally purified by a process involving the crystallisation of thorium sulfate from purely sulphuric solutions. The details of this process[4] which permits also the recovery of the uranium contained in the crude thorium hydroxide, have already been described elsewhere. Final purification to a "gas mantle grade" thorium nitrate or oxide is achieved by precipitating thorium sulfate from chloride solutions[5].

A solvent extraction process, using tributyl phosphate—kerosene mixtures as solvent for thorium nitrate is being studied at present on a pilot plant scale. It seems, that a thorium product of a purity better than 99.99% can thus be obtained starting directly from the crude thorium hydroxide.

The bulk of the rare earths is actually used as mixture in their natural composition in the form of their chlorides, double sulfates or optionally carbonates or oxides. The final aim of the Brazilian industry is, however, to split this mixture into the individual components in the most economical way, actually possible. Considerable progress has been achieved in the past few years due to an extensive research program developed in this direction.

It is obvious, that the successful development of applied and technological research is hardly possible without the pursuit of fundamental research. This research is directed essentially towards the physico-chemical properties of rare earth compounds and especially towards their behaviour in complex formation.

The successful study of separation methods depends greatly on the availability of rapid and precise analytical methods. The spectrophotometric method for the determination of the rare earth elements has been brought to a high perfection and new equipment has been developed for that purpose[6]. The spectrophotometric method is supplemented, especially in the case of very complex mixtures, by ion exchange separations and by precise determinations of the atomic weight.

Brazilian industry was the first to produce Europium oxide of 99% purity on an industrial scale, using a modified Mc Coy Process[7].

The yttrium and ytter earths concentrate, resulting from the double sulfate process is already separated on an industrial scale into a crude yttrium oxide (75 to 80 % Y_2O_3) and a gadolinium concentrate with about 50 % Gd_2O_3. This and the separation from the bulk of the cerium earths, contained in the crude concentrate is achieved by a series of double sulfate precipitations.

The production of pure yttrium oxide and of ytter earths oxides by means of ion exchange has been studied extensively and very successful new methods have been developed. Yttrium oxide of high purity has already been produced using columns of 30 cm diameter. The same is true for Ytterbium, Erbium and Dysprosium oxide, which were obtained in a purity of better than 98%.

A new reduction process for samarium has been elaborated on a laboratory scale and will be tested in the near future in a pilot installation.

Considerable progress has been achieved, too, in the separation of the cerium earths, especially of lanthanum. Cerium is separated from the trivalent earths in the usual way, by oxidation and subsequent solubilisation of the trivalent earths. Lanthanum is separated in a very good yield and high purity by precipitation with ammonia. The conditions of the ammonia precipitation have been very extensively studied in a large pilot installation (batches of 400 to 500 kg. of oxides) and the problem of the filtrability of the hydroxides overcome in a very satisfactory way.

The studies of the industrial separation of the rare earths are continued in the laboratory and the pilot plant scale in all directions, including separations by means of solvent extractions.

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APPLICATIONS OF RARE EARTH METALS IN METALLURGY

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Between barium (Group II) and hafnium (Group IV) in the perodic Table occurs a group of fifteen chemically similar elements known as the rare earths.

Atomic No.		Atomic No.	
57	Lanthanum	65	Terbium
58	Cerium	66	Dysprosium
59	Praseodymium	67	Holmium
60	Neodymium	68	Erbium
61	Promethium	69	Thulium
62	Samarium	70	Ytterbium
63	Europium	71	Lutetium
64	Gadolinium		

39 Yttrium, 90 Thorium } Not rare earths, but always occur with them.

The choice of the term 'rare earths' to designate these elements arose from their relative scarcity at the time this name was proposed and from the position that their oxides resembled the alkaline earth oxides. Because of this unique similarity, the rare earths have been the source of much fruitful work on the electronic structures of the elements. For the same reason, these elements provide vast scope to evaluate existing theories of metals and the relations between their properties and electronic structures.

For many years, the principal uses of the rare earth metals were based on their pyrophoric nature. The only satisfactory lighter flint is a rare earth iron alloy. The largest use of misch metal is in lighter flints, but the use of misch metal in alloys now compares favourably with its lighter flint use. Until mid-1954 rare earth supply and demand were about in balance, but a noticeable surplus has been piling up since then.

The most important source of the rare earths in India is the vast deposits of Travancore beach sand. The mineralogical composition of the beach sand is :

	Manayalakurichi	Neendakara
Ilmenite	75-80%	80%
Zircon	4-6%	4-6%
Sillimanite	2-4%	3-5%
Rutile	3-5%	4-5%
Garnet	3-5%	Less than 0.5%
Silica	5-7%	4-5%
Monazite	About 1%	0.5 to 1%
Other minerals less than	0.1%	

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The Analysis of a pure monazite sand is given below :—

	(%)
U_3O_8	0.273-0.35
CeO_2	27.82
P_2O_5	23.82-29.1
La_2O_3	14.25
Nd_2O_3	9.546
ThO_2	7.36-9.5
Pr_2O_3	2.64
Sm_2O_3	0.91
Oxides of other rare earths, Y_2O_3 etc.	0.90

besides silica and other impurities

Relative analyses of pure monazite from different parts of the world are given below : (%)

	India Travancore	Brazil Espirito Santo	Malay Pahang	Perak	Australia Byron Bay N.S.W.
Thoria, ThO_2	8.1	6.06	8.38	3.49	7.20
Ceria, Ce_2O_3	30.6		24.56	33.74	27.1
Lathanum oxide, La_2O_3	15.7				
Praseodymium oxide Pr_2O_3	2.9		37.72	32.83	32.9*
Neodymium oxide, Nd_2O_3	10.5	62.12			
Europium, Gadolinium and terbium oxides	0.7				
Yttrium oxide, Yt_2O_3	0.4				
Dysyprosium, holmium, erbium, ytterbium and lutetium oxides	0.1	0.80	2.80	0.91	

* Includes other M_2O_3 rare earth oxides.

In the last few years, considerable interest has been aroused in the use of rare earth metals in both ferrous and nonferrous alloys. Perhaps it will not be out of place to give a few of its topical applications:

Misch metal is successfully used in basic electric or open hearth steels. Steels properly made with 1.5 lbs aluminium, 2 lbs misch metal, and 3 lbs calcium-manganese-silicon per ton have good low temperature impact resistance. Cracking caused by forging in such steels is considerably less than in steels not containing rare earths.

In cast iron, misch metal addition to the ladle in some applications favourably affects fluidity, hot workability, oxidation resistance and strength. About 4 lbs of misch metal per ton of molten iron added prior to casting results in the conversion of flake graphite into nodular graphite.

Rare earth oxide and rare earth fluoride have been used in place of the metal, particularly in stainless steels and to some extent in acid open hearth steels. The hot workability of austenitic steels containing 4-40% nickel is improved by adding misch metal upto 0.2%. The additions of rare earth metals to austenitic stainless steel and high nickel alloys render these alloys which were previously unworkable even when hot thus necessitating their use only in cast forms, now fully forgeable with high yield figures and with excellent surface properties.

The addition of misch metal (1.3-11%) in light metals and alloys such as aluminium and magnesium alloys increases the high temperature strength properties of these alloys. Several alloys have been developed e.g., the addition of about 0.3% rare earth metal to aluminium-copper-silicon piston alloys; the use of 0.05-0.3% rare earth metal in aluminium alloys containing manganese and the recent use of rare earth-zirconium-magnesium alloys for jet engine parts. Rare earth metal can be used as a deoxidiser in copper and copper alloys; it is equal to magnesium, and better than aluminium or silicon for this purpose.

Cerium is also said to be of beneficial influence in aluminium production, and to increase the toughness of pure aluminium by reducing the silicon contents. It is claimed that an addition of 0.2% cerium will reduce a silicon content of 0.1% to 0.02%. For this purpose cerium should be added to the aluminium in the fused state, perferably in the form of a high cerium containing aluminium alloy, or in the form of cerium fluoride to the electrolytic bath in which aluminium is prepared.

According to an American invention a copper alloy containing between 0.1 and 1% cerium, 5 to 10% aluminium, and balance copper has superior characteristics over other metals at present used in bearings, and is particularly suitable for shafting subjected to severe service and heavy loads. This alloy radiates heat so rapidly that relatively close clearances can be obtained and is capable of running with the minimum amount of lubrication.

In amounts from 0.02 to 0.2%, the rare earths greatly improve the oxidation characteristics of nickel-chromium alloys such as the 80-20 wires and grids used for electrical heating elements. The preferred additions consist of a few hundredths percent alkaline earth metals, preferably calcium, along with 0.15—0.2% of rare earth metals, preferably cerium. Similar results are achieved by the introduction of calcium 0.03% residual, thorium (say 0.07%) and a few hundredths parts percent of phosphorus, arsenic or antimony. As alloying elements in amounts of the order of 1 to 3%, the rare-earth metals have raised the creep resistance of magnesium-base alloys and thus allowed the use of these alloys at elevated temperatures in aero-engine development.

The advantages of the additions of misch metal were observed in alloy steel mill practice when it became apparent that improved yields from ingot to finished wrought product could be obtained from many of the standard stainless steel grades. The highly beneficial effects of minute additions of rare earths are pronounced chiefly in high alloy steels and stainless steels.

Rare Earth Additions to Stainless Steels

The rolling qualities of stainless steel are determined by a number of metallurgical factors, chief of which are the structure and grain size

of ingot, pouring temperature, the influence of additions of small amounts of special alloying elements, and the phase in which the steel has solidified (ferritic or austenitic). The 'rollability' of straight-chromium ferritic and martensitic, chromium-nickel austenitic, two-phase complex chromium-nickel, and chromium-manganese steels is not the same.

The martensitic and ferritic steels hot-roll easily and no special additions are required to promote workability. Austenitic steels are more difficult to hot-roll, being characterised by two types of hot-shortness, one due to a duplex austenite-ferrite structure, the other inherent in the higher-alloyed steels of this type. Hot-shortness due to duplex structure can be prevented by correct balance of the constituent elements, by judicious selection of the hot-rolling temperature, and by soaking for adequate periods at suitable temperatures prior to hot-rolling. The inherent hot-shortness found in the higher-alloy austenitic stainless steels increases with the size of the ingot, and is considered to be related to coarseness of grain. Addition of a deoxidizing ferro-alloy, containing substantial proportions of titanium and aluminium, effects some improvement, but hot-shortness is best counteracted by the addition of rare earths, in metal or oxide form. Experiments with rare earth metals done by Henke and Lula[1] showed that best results are obtained by the use of 4-5 lb. of rare earths. When used in amounts of about 3 lb. per ton, in steel already treated with a deoxidising ferro-alloy, or to the extent of 5 lb. per ton in steel not previously treated with a special deoxidizer, highly successful results are obtained. Cerium was the most potent constituent in the rare earth oxide addition, and there appeared to be, from the point of view of hot-workability, an optimum amount of rare earth oxide addition, expressed as 0.036-0.040 per cent cerium.

Work carried out by the Allegheny-Ludlum Steel Corporation in U.S.A. has proved the use of rare earth oxide additions to be so advantageous that it has been adopted as standard in their plant, whereby ingots for which a two-stage conversion was previously necessary can now be hot-rolled in a single stage. Ingot yield has also been shown to have markedly improved by this treatment.

Evans[2] has summarized the effects of rare earth metals additions on austenitic and ferritic steels as follows :—

"During the past four or five years other important effects have been attributed to the rare earth metals, for example, increased ductility, at forging and rolling temperatures, of austenitic steels and improved mechanical properties of ferritic steels, resulting from the addition of misch metal or Lan-Cer-Amp. In the U.S.A., from where most of the published information on this subject has emanated, these developments have been acclaimed as two of the most important in the ferrous field during the last half-century. With regard to the stainless steel field, treatment of the molten steel by misch metal is reported to effect consi-

derable improvement in the hot-workability of the austenitic types. In other grades, such as 19|10 chromium-nickel, 22|12 chromium-nickel and 16|10|2 chromium-nickel-molybdenum, which are not considered exceptionally difficult to hot work, the addition of misch metal has increased which amply compensates for the cost of the rare earth metal addition. Furthermore, the appearance of the edges and the surfaces of the hot-finished strip are more satisfactory, and require less grinding. It has been found that for this purpose residual contents of the order of 0.02 to 0.15% of rare earths are required in the steel. The more outstanding effect of the rare earths is evident in the more highly alloyed stainless steels. Although steels such as those containing 20% chromium, 25% nickel, 3% molybdenum and 3% copper, required for exposure to severely corrosive conditions, have been available in the form of castings, only small quantities have been produced in wrought form, due to the poor hot-workability of this steel. Treatment of such steels with misch metal, to give a residual content of about 0.20% rare earths, has made possible rolling to plate and strip with a reasonably good yield. There is a critical range of cerium and lanthanum contents required to obtain the best hot-working properties, and that the maximum amount of rare earth metals essential for maintenance of hot-workability decreases as the nickel content increases.

As an alternative to misch metal, austenitic steels have been successfully treated with rare earth metal oxides in the form of 'T' compound, added together with suitable reducing agents, such as calcium boride and sodium nitride. Although the hot-workability of the lower-alloy austenitic steels has been improved by such treatment, there is some doubt whether this mixture is effective in the more highly alloyed steels. Addition of cerium fluoride have also been found to improve hot-workability, but only in the lower-alloy austenitic steels containing titanium. In contrast to the residual amounts of cerium and lanthanum in the finished steels treated with misch metal, no rare earth elements were found in the steels after treatment with the oxide or the fluoride which probably accounts for the relative ineffectiveness of the alternative addition agents.

The mechanism for the improvement or promotion of hot-workability of austenitic steels by treatment with misch metal is also not clearly understood. It is thought that such additions will completely deoxidise the melt, a condition which could contribute to improved hot-workability. Further, it is known that rare earth metals, when present in sufficient amounts, can prevent the hot-shortness developed by sulphur, but it is also possible that, as in cast iron, the rare earth metals act as 'scavengers' and counteract the harmful effects of subversive elements such as lead, titanium, tin and silver, which are known to impair the working of stainless steels.

H. O. Beaver[3, 4] and C. B. Post and H. O. Beaver[5] have established the following advantages when stainless steels are alloyed with minute amounts of misch metal ;—

New wrought alloys with unusual properties are produced : Hot working improvements obtained with misch metal additions have led to the development of alloys which could not, under ordinary circumstances be manufactured commercially particularly sulphuric acid resisting wrought stainless steels. Carpenter Austenitic stainless steel No. 20 containing 20 Cr, 29 Ni, 2 Mo and 3% Cu which could be previously made available only in cast form can now on misch metal additions be produced in wrought bars, stripsand wire, sheet etc., and it is the only wrought stainless steel which resists corrosion by hot sulphuric acid-boiling concentrations to 10% and resist all concentrations at 175 deg. F.

Improvements in mechanical properties of stainless steels : In addition to improved hot-working properties, rare earth additions improve mechanical properties of austenitic stainless steels such as high temperature strength and ductility—a misch metal addition of 4 lbs|ton of stainless steels will improve stress rupture properties by a factor 25% at the 100-hour life level.

Hot-working properties are improved ensuring lower fabricating costs: Many standard stainless steels e.g. types 310 and 316, presented serious problems in forging and hot working properties. Certain forged shapes were practically impossible to produce from these steels and others were made with poor yields and high rejection rates. The misch metal alloy additions improved the forgeability generally of these steels but more significantly it broadened the forging temperature range.

The rare earth elements definitely have a worth-while place in the production of wrought stainless steel alloys and other high alloys as well Of course, they are not a cure-all, and do not substitute good melting practice in producing optimum hot workability and physical properties.

Similar treatment with rare earth metals has been found to have a beneficial effect on the ductility and toughness, at ordinary and sub-zero temperatures of cast carbon and low-alloy steels[6]. Reports of the work carried out in the field indicate that misch metal and Lan-Cer-Amp are employed; either is added after deoxidation of the steel with aluminium. Lan-Cer-Amp, containing 30% or more of lanthanum, has been claimed to be more potent than misch metal in its beneficial effects on carbon and low-alloy steels. The influence of this treatment for a cast 0.24% carbon steel in which it will be noted that, by adding 4 lb. of misch-metal per ton of steel, the elongation, reduction of area and impact values are increased, and, further that the higher level of impact properties is maintained at sub-zero temperatures. Similar improvements in these properties are obtained also in cast low-alloy steels after quenching and tempering to any hardness level. In addition to the beneficial influence of rare-earths on the mechanical properties of cast steels, it has been reported that the fluidity of the treated steels is increased, while the susceptibility to hot tearing is reduced.

Published work shows, that the hardenability and susceptibility to temper-brittleness are not affected by rare earth treatment.

Aluminium-killed steels required for green sand mould castings are very susceptible to the formation of intergranular films of sulphide, which must obviously have an adverse effect on the ductility and toughness of the steel. The addition of rare earth metals, as also of tellurium and selenium (which are not in the rare earth group), raises the freezing temperature of the sulphide phase and consequently enables the sulphide to precipitate earlier in the solidification process, in the globular form instead of as inter-granular films. This is undoubtedly one of the reasons for the improved mechanical properties of rare earth treated cast steels. Further, due to the desulphurizing effect of the rare earth metals, steels treated in this way show a lower sulphur content than an untreated steel, which must be recognized as a factor contributing to the improvement in properties. The ability of the rare-earths to deoxidize and to remove nitrogen and hydrogen from steels is probably an additional contributory factor, which has to be taken into account.

Rare Earth Addition to Cast-Boron Steel

Cerium[7] rare earths have been found to increase the impact strength of quenched and drawn cast boron basic electric steel of the composition :

C	..	0.28	—	0.34%
Mn	..	1.1	—	1.7 %
Usual Si, S & P.				

The beneficial effect appears to decrease with decreasing temperature. Apparently rare earths do not directly increase hardenability. Half of each steels treated with rare earths has a hardenability greater than the half not treated with rare earths. A 35-45% increase has been obtained in 3-6 heats containing 0.009-0.016% N. It is known that this level of N inhibits the boron effect in improving hardenability.

In case of a normalised high tensile, low C, low alloy steel of the composition C—0.1-0.18%; Mo—0.4-0.6% by adding boron to it, UTS increases from 45,000 to 65,000 psi with good impact strength at low temperatures. This drawback can be overcome if further tests substantiate the results of one heat to which 0.10% rare earths were added. The cerium rare earths increased the impact from 8-18 ft-lb. at -40° F. Misch metals have been used in boron steels with interesting results. For example, 3 to 15 lb. of misch metal added to a ton of 8,640 steel increased the impact strength from about 30 ft-lb upto between 40 and 50 ft-lb.[8]

W. E. Knapp and W. L. Bolcom[9] have shown that small additions of Lan-Cer-Amp (the rare earth addition alloy produced by American

Metallurgical Products Company) give consistently higher toughness and ductility values in steels quenched and tempered to a given hardness level in low alloy Cr-Ni-Mo steels. Improved low-temperature impact strengths are of added importance since they are a measure of susceptibility to notch sensitivity and shock resistance. Lan-Cer-Amp has increased the -40° F. V-notch impact values of a wide variety of low alloy steels by over 50%. In one instance, transverse -40° F. V-notch values for 0.32C Cr-Ni-Mo forgings, quenched and tempered to 400 BHN were raised from an average of 12 ft-lb to 20 ft-lb. Cr-Ni bars, quenched and tempered to 250 BHN showed the following improvement in -40° F. V-notch tests :—

	Untreated (ft-lb)	Treated (ft-lb) (2 lb per ton)
Longitudinal . .	56	85
Transverse . .	36	55

Transition temperature lowered

In this particular case it was found that the addition lowers the impact transition temperature from about -150° F. to about -250° F. The transition temperature is that temperature below which the fracture at the base of the notch changes from fibrous to granular, occurring usually at an impact level of 10 to 12 ft.-lb.

It is generally conceded that, other factors being equal, low oxygen, low nitrogen, low hydrogen and fine grain are instrumental in increasing low temperature impact strength. From previous discussions in this article it should be evident that all of these conditions may be induced in steel through Lan-Cer-Amp additions in the absence of strong nitrogen fixers. Since nickel has long been advocated as an agent for increasing low temperature toughness, it should be pointed out that an addition of 2 lb. per ton of Lan-Cer-Amp is as effective in this regard as 2% Ni.

Lan-Cer-Amp used in quantities of 1 lb. per ton or less definitely improves the working characteristics and, consequently, yields of high speed steel by 5 to 10%. Another rather specialized application has been in an airhardening alloy containing 7.0% Mo, 3.0% Ni, 3.0% Cr, 0.60% 'C. 0.40% Mn, 0.25% Si and 0.50%. Boron and produced in a basic electric furnace. Originally it was necessary to cast the material to shape because of its extreme hot-shortness. With addition of 4 lb. per ton of Lan-Cer-Amp. the alloy, after forging, rolled easily into 7|16 in. rod. It was then coiled with yields comparable to 18-8.

Lan-Cer-Amp additions have also increased the semi-finished-slab yield silicon electrical grade steels particularly on very wide sheets and have permitted rolling up to 2½% Si sheets in widths 12 to 24 in. greater than previously possible. The total core loss (Epstein test)

of experimental sheets was reduced from 1.25 to 1.0 watts per lb. at 60 cycles by additions of 2 lb. per ton. The use of rare-earth metals in electrical grade steels having unusually low total watt losses was first proposed by Rohn and Hessenbruch in United States Patent No. 2144200.

One of the reasons that the rare earth metals have remained dormant so long is that the proper conditions necessary for successful use were not known or observed.

G. Cheetham[10] of London and Scandinavian Metallurgical Company Limited, Sheffield has summarized the existing data on both rare earth metals and rare earth oxide additions in stainless, low-alloy, silicon and other types of steels. In U.S.A. in consequence of rare earth additions, the use of rare earth oxide additions is becoming widely adopted in the SAE 308, 309, 310 and 316 types of steels in amounts varying from 1½-5 lb. per ton of steel. Some American steel works, having standardized the use of rare earth oxides in the production of the common grades of stainless steel, are now able to produce economically 20 ton ingots where so far 4 ton ingots had been the maximum. At the same time the rolling yields of 75% are now being obtained against the 65% obtained with the 4 ton ingot not treated with rare earth oxides.

G. A. Lillieqvist and C. G. Mickelson[11] have reported a systematic investigation of the influence on the properties of typical plain and low-alloy (manganese) cast steels, of additions of Lan-Cer-Amp. Individual sections of the report cover the effects of Lan-Cer-Amp on mechanical properties, temper-brittleness, inclusions and microstructure, fluidity, susceptibility to hot-tearing, removal of sulphur, hardenability, porosity, weldability and feeding characteristics.

H. Schwartzbart and J. P. Shoehan[12] have investigated the use of proprietary mischmetal additions at the Armour Research Foundation in U.S.A. and have shown that such additions can increase toughness without affecting the hardness of 4330 steel of the composition :

C	...	0.27 — 0.29%
Mn	...	0.70 — 0.76%
Si	...	0.2 — 0.3 %
P	...	below 0.02%
S	...	upto 0.02%
Ni	...	1.5 — 1.6 %
Cr	...	1.6 — 1.8 %
Mo	...	0.18 — 0.2 %

They concluded that resulting improvements in transverse impact properties could reduce service failures. Although the cost of rare earth additions is high, future potential is promising where optimum mechanical properties are required such as in aircraft parts.

Applications of rare earths in non-ferrous alloys

The use of rare earth metals in non-ferrous alloys has aroused considerable interest during the last few years. Such metallurgical applications of rare earth may be classified in two broad headings :—

1. Applications in which rare earths form an alloy with some other metal e.g. with aluminium and magnesium.

2. Applications where rare earths play a weak role as alloying agents but function fundamentally as purifying elements.

In each case rare earths are added in the form of a mixture and not in their pure state. Two types of mixtures are widely used one of which is Lan-Cer-Amp (Lanthanum, cerium) whose average analysis is as follows :—

Lanthanum	...	30%
Cerium	...	45 to 50%
Mixture of neodymium	...	20 to 24%
Praseodymium & Sumarium *and* Iron	...	10% max.

The other mixture is misch metal which is derived from monazite and contains 22 to 25% lanthanum, 50 to 55% cerium, 15 to 17% neodymium, 8 to 10% other rare earth metals (varying according to origin of monazite). ([15])

Rare earths are chiefly used in non-ferrous alloys of aluminium and magnesium. 10 to 12% of the Lan-Cer-Amp or misch metal added to aluminium will considerably improve its mechanical resistance to heat. However, additions of rare earths required for magnesium are not so large. A few percent of rare earths added to magnesium improves its mechanical resistance to heat, refines the grain structure and produces a more easily workable material.

Leontis[13] has evaluated the specific effects of various rare earth metals at room and elevated temperatures on properties of magnesium. Alloys containing didymium exhibited the highest tensile and compressive strengths at room and elevated temperatures. All rare earth metals increased the creep resistance of extruded magnesium between 400 to 600 deg. F., but the increase depended on the temperature and the concentration of the added metal.

Magnesium rare-earth metal alloys were investigated in Germany many years ago and the findings were published in Becks Technology of Magnesium in 1939. Cast alloys of magnesium with rare earths have now become commercially available. They all use zirconium as a second essential alloying element because of its grain-refining effect, thus preventing cracking during freezing.

For aircraft applications, engineers and metallurgists have sought alloys with high strength-weight ratio and ability to withstand increasing stresses at elevated temperatures. Patton[14] has described that by adding 2 to 4% rare-earths to Mg-Zr alloys, Dow Chemicals have obtained new alloys with outstanding high temperature properties.

At 300 deg. F. and above, cast magnesium-zirconium alloys with 2 to 4% additions of rare earth metals, have shown as much as five times the creep strength compared to older magnesium-aluminium-zirconium type alloys. For aircraft engines which require outstanding elevated temperature properties and high strength-weight ratios, the properties exhibited by these alloys with rare earth additions are particularly useful. Several alloys have been developed e.g. the addition of 0.3% rare earths to aluminium-copper-silicon piston alloys, the use of 0.05 to 0.3% rare earth metal in aluminium alloys containing manganese and the recent use of rare earth zirconium alloys for jet engine parts. The latter alloys contain 0.1 to 0.9% Zr and upto 4% rare earths and sometimes 1 to 6% Th and 0.5 to 5% Zr. The didymium metals, particularly neodymium, are especially interesting in this application but their use may be restricted due to limited availability of neodymium. Misch-metal contents upto 11% in an aluminium alloy containing silicon, copper, nickel, manganese and small amounts of chromium and titanium have been recommended for high temperature aircraft engine service.

In nickel alloys, additions of 0.2 to 2% rare-earth metal improves the high temperature oxidation resistance. An interesting application[15] of rare earths is in connection with heating elements e.g. nickel-chromium 80|20 alloys and alloys containing iron, chromium and aluminium. This has already been referred to. Another interesting application of rare-earths is in its use as deoxidiser in copper and copper alloys. It has been observed that rare earths function better than aluminium or silicon for this purpose and are as good as magnesium.

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Discussions

Mr. L. M. Wyatt, (*U. K.*) : I would like to call attention to the possible future use of rare earths as control absorbers in nuclear reactors. Gadolinium and europium have very high neutron absorption cross-sections, and are free from the particle production of boron.

Europium has the further advantage that the higher isotopes formed by neutron absorption are themselves good absorbers, so that its efficiency as an absorber is retained for a long period.

The materials will probably be used in the form of oxide dispersions in steel.

THE PRESENT STATUS OF ZIRCONIUM METALLURGY

*By Brahm Prakash and C. V. Sundaram**

Even a decade or two ago, zirconium was a rarity of little known engineering properties and potentialities, selling at a fabulous price of $315/lb. which indicated a sluggishness of development, mainly conditioned by difficulties arising from the high melting point of the metal and its extreme reactivity in the molten state. In 1948, the Kroll process for producing zirconium sponge by protected magnesium-reduction of redistilled, anhydrous zirconium tetrachloride was getting established at the U. S. Bureau of Mines Station at Albany, Oregon but the quality of the sponge was such that it needed further refinement by the iodide dissociation process to obtain ductile zirconium crystal-bar. About this time, it also came to be recognised that hafnium-free zirconium has an attractively low neutron capture cross section, and this, combined with its corrosion resistance and desirable mechanical and fabrication characteristics, marked it out as an ideal structural material for reactor applications. Since then, in the short space of less than a decade, there has been an almost explosive expansion of the zirconium industry, especially in the United States. By 1952, the Kroll process sponge had improved in quality and production at Albany had gone up to nearly 300,000 lbs/year. Construction of a completely integrated production plant capable of turning out 150,000 lbs. of reactor grade zirconium sponge per year, at a selling price of $15 per lb. was completed by the Carborundum Metals Co., Akron, N. Y. by mid-1953. This year also saw the first major industrial use of zirconium in the fabrication of the high-pressure, high-temperature, water-cooled and moderated reactor for the atom powered U. S. submarine Nautilus.

Metallurgical compatibility with uranium, resistance to corrosion by water and liquid metal coolants, and to radiation damage, retention of strength to moderately high temperatures, and favourable response to alloying modifications are some of the factors that have placed zirconium on an even firmer footing in reactor engineering in more recent years. With improved melting and fabrication techniques and with the development of new zirconium base alloys, industry's confidence in the future of zirconium is getting confirmed. The intricate-shaped core tank for the Homogeneous Reactor Test at the ORNL has been fabricated entirely out of an alloy of zirconium.[1] In the experimental sodium-graphite reactor, designed for operation in the temperature range 260-515°C, zirconium sheet cladding is provided for the hexagonal graphite prisms as shield against liquid sodium, and the lining of the coolant channels is all of zirconium metal.[2] Fuel element seed assemblies for the 60 megawatt pressurised water reactor (PWR), Shipping port, Pa., employ zirconium-uranium alloy plates sandwiched in zircaloy-2, with a blanket of UO_2 pellets encased in zircaloy-2 tubing.

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U.S. production capacity for zirconium, which stood at 625,000 lbs./year by the end of 1956, is expected to reach an estimated 5,000,000 lbs. annual rate by 1960, with new plants going on stream[3]. The U.S. AEC is now on a 5 year contract with three different producers for the supply of 2,525,000 lbs. of zirconium/year under a 14 million dollar programme which excludes another 300,000 lbs. of metal to come from the reactivated Bureau of Mines plant at Albany[4].

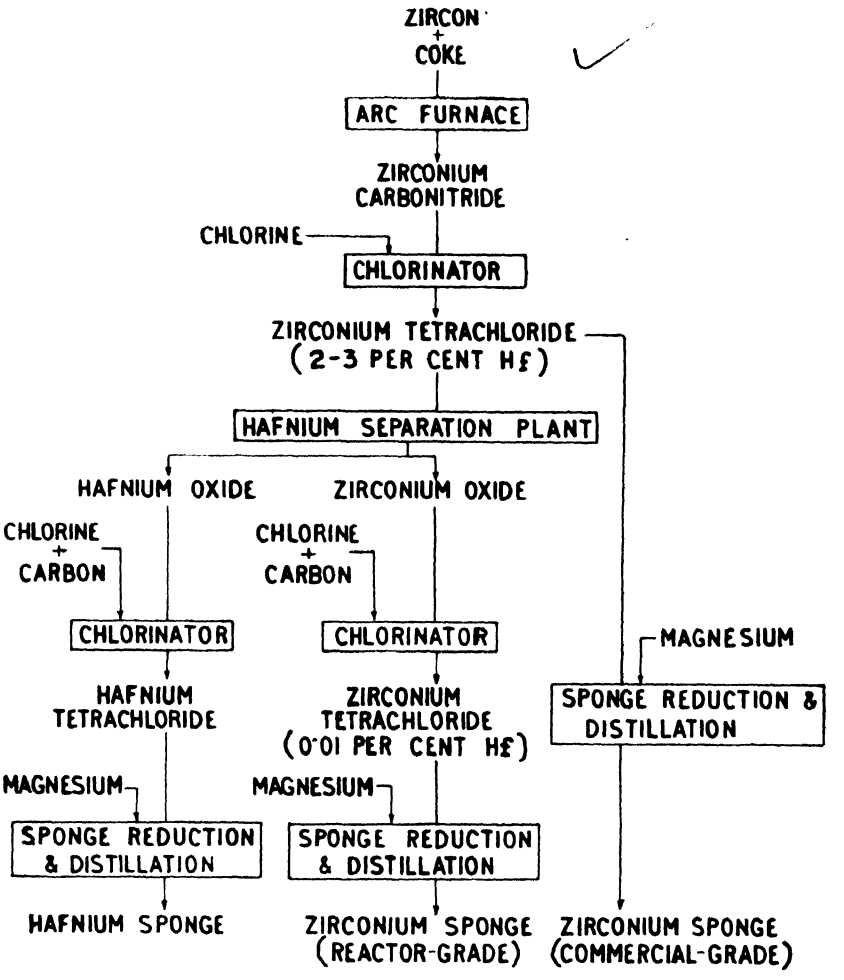
In the United Kingdom, where development of atomic energy has centred mainly around gas-cooled reactors, zirconium production has been modest. The annual output was about 20,000 lbs. from the Murex Ltd. Reinham, though more intensive research with zirconium alloys is expected to stimulate greater interest in the metal[5]. The only other country at present producing zirconium on a commercial scale is Japan, which has offered to supply the U.S. AEC with 200,000 lbs. of reactor grade sponge at competitive rates. Pilot plant production work is reported from France and Germany. The figures of production in U.S.S.R. are not available.

Zirconium technology has followed a rather unusual pattern, as the emphasis from the very beginning has been on a hyper-purity material for specialised applications. All the same, the long term objective of producing commercial grade metal, cheap enough for general and more widespread acceptance, is being kept up. Though no successful approach is yet evident in the development of a continuous production process, better utilisation of existing plant equipment and streamlining of production operations have brought about substantial reduction in costs. The sequel discusses some of the recent developments.

The Kroll Process and its modifications

Commercial production of ductile zirconium, today, is almost entirely by the Kroll process, the success of which depends on the use of oxide-free, redistilled zirconium chloride and the exclusion of air in the crucial magnesium reduction step. The various stages in the development of this process are discussed in great detail in many recent publications[6],[7]. The principal steps adapted for the production of reactor as well as commercial grade zirconium sponge, are indicated in the accompanying flow sheet[8].

Briefly described, the Kroll process, in its earliest form, included a prior purification step wherein crude zirconium tetrachloride was sublimed in a hydrogen atmosphere, at a slight positive pressure, and condensed on to water-cooled coils suspended from a cover that floated in a molten Pb-Sb seal, on top of the retort. The dense mass of condensed chloride was then transferred to the magnesium reactor and the chloride was resublimed in helium and reduced in a crucible containing molten magnesium. The reaction product which consisted of fine zirconium crystals surrounded by magnesium and covered by magnesium chloride was either leached with dilute acid or preferably sub-



jected to vacuum distillation to remove magnesium chloride and residual magnesium, yielding a sponge-like product of the sintered metal.

It was, however, eventually demonstrated that the preliminary purification step can be dispensed with, by allowing the crude zirconium chloride to outgas at a reduced pressure below its normal distillation point. Purification and reduction have since been combined into one operation cycle in a single furnace thereby effecting a 30% saving in time and considerable reduction in cost and equipment without sacrifice of quality or efficiency.[9]

The reduction step itself was a delicate operation calling for considerable manipulative skill, as the floating top restricted pressure varia-

tion inside the reator to a tolerance of 0.3 p.s.i.g. Excessive pressure inside forced the gases through the seal, causing the molten alloy to sputter all around, while a fall in pressure encouraged leakage of air into the reactor leading to deleterious contamination of the metal.

More recent investigations have established that the reduction process can be adapted to an automatically controlled cycle, if the conventional floating top is replaced with a rigid, immobilised seal and pressure fluctuations inside the retort are taken advantage of in controlling the progress of the reaction. Continuous, reliable measurements of the retort pressure can be used to actuate conventional pneumatic control instruments which will (i) deliver cooling air to the condensing coils in proportion to the amount of pressure imbalance, (ii) bleed process gases from the retort, (iii) control the furnace resistors to sublime more or less of $ZrCl_4$, and (iv) add helium gas as and when it is necessary[10]. Such an automatic control has been found to simplify operation without adversely affecting product quality.

The Kroll process, however, is essentially a batch process with inherently high labour costs and even with rigid control, there is an inescapable variability in impurity content from batch to batch. Attempts to convert it at least into a semi-continuous process have hitherto been non-too-successful for various reasons. Continuous drainage of magnesium chloride as it is formed, with provision for intermittent addition of liquid magnesium has been suggested for doubling up reduction crucible capacity[9] but then, there is the associated risk of exposing the zirconium sponge to direct reaction with $ZrCl_4$ which would lead to the formation of viciously pyrophoric $ZrCl_2$. A recent innovation that shows promise of cost reduction and improvement in quality, involves the use of a thin sheet of high carbon steel as a liner for the reduction crucible. At the end of the reduction step, the metal liner can be stripped off and the reaction mass broken up to remove most of the magnesium chloride mechanically. This would allow better utilisation of furnace capacity in the distillation step.

Sodium reduction of zirconium tetrachloride

In a discussion of the use of sodium as a possible substitute for magnesium in the reduction of zirconium chloride, Kroll[11,12] has indicated that the low boiling point of sodium (880°C) and the relatively high melting point of sodium chloride (801°C) would give only a narrow temprature range for operation, if the vapourisation of sodium is to be avoided. Further, the greater exothermicity of the reaction with sodium introduces heat dissipation problems and the larger volume of salt obtained in the reaction chamber would curtail production capacity. On the other hand, the use of a mixture of sodium and magnesium as the reducing agent would have some advantage as it would give a low melting salt mixture as the reaction product, which would also be less hygroscopic than pure magnesium chloride.

It is now reported from the United States that the National Distillers Corporation, who are on a contract with the U.S. AEC for the supply of 1,000,000 lbs./year of reactor grade zirconium at $4.53 per lb. have adopted sodium reduction in their production line[13]. The price of sodium today, on an equivalent basis, is practically equal to that of magnesium in the U.S. Sodium is easier to clean and offers a technical advantage in that it can be piped to the zone of reaction under control. It is claimed that sodium gives even a purer product than magnesium and plant equipment costs are only 40% as much as for the Kroll process. It was originally thought that since sodium is the reducing agent, a simple water leach would give a clean sponge. Experience has however shown that an extra induction melting step is necessary to get rid of the impurities.

The dense sponge from sodium reduction is ground to ¼" size and leached with water to remove most of the sodium and NaCl. The leached material which still contains 0.3% NaCl and 0.02% sodium is induction melted under argon in order to vapourise the salt and the residual sodium. Molten high purity zirconium is allowed to drip on to a whirling disc where it quickly solidifies to form irregularly shaped 1" dia. platelets. The platelets are considered to be easier to handle than sponge and do not present any fire hazards.

The Iodide-process

At a stage when the Kroll process sponge was still high in impurity contents, particularly oxygen and nitrogen which seriously impair its ductility and corrosion resistance, the U.S. A.E.C. requirements of superpurity zirconium were being met entirely from crystal bar supplies from the Van Arkel-de Boer iodide process.

This process, which produced the first truly ductile zirconium in history (in 1925), is a refining and consolidation process starting with crude sponge or metal powder, and is based on the reversibility of the reaction between zirconium and iodine.

$$\mathrm{Zr(Crude\ Solid) + 2\ I_2(g) \xrightarrow[200^\circ C]{} ZrI_4(g) \xrightarrow[1300^\circ C]{} Zr\ (Pure\ Solid) + 2\ I_2(g)}$$

When American rights for the process were acquired by the Foote Mineral Co., Pa., from the Philips Lamp Works, Netherlands in 1940, the glass bulbs used in the early stages were substituted with metal reaction vessels of inconel which gave increased production capacity, improved temperature control and better manoeuvrability. In the further expansion of the project, in 1950, at the Atomic Power Division of the Westing-House Electric Corporation, Hastealloy B came to be adopted for its more satisfactory corrosion resistance. Also, in order to avoid necking at filament supports and provide additional anchorage and greater current carrying capacity for larger crystal bars, special-shaped electrode transition tips were designed, with the help of which it was possible to produce zirconium bars weighing as much as 117 lbs.

The principal attraction of the iodide process has been in the exceptional purity of the crystal bars, though there is this qualification that the latter are as much susceptible to impurity pick-up during the melting stage, which has to precede fabrication.

A major deterrent, however, to the large scale expansion of this process is its poor economics, arising from the fact that it employs costly zirconium sponge as starting material and on this basis it can never compete with the Kroll process. Zirconium powder from the calcium or magnesium reduction of the oxide would be a cheaper feed material. It has been also suggested that if the iodination and dissociation steps are separated, the process might be adapted to continuous operation with considerable reduction in costs.

A fascinating account of research and development work on the iodide process has been presented by Shapiro[14]. In summing up the present situation, he says 'Continuous processes (like 'arc-dissociation,' 'cyclical flow', and 'film-boiling') have real merit. Their application could result in significant savings which might indeed make iodide zirconium competitive with zirconium produced by any other method. Nevertheless, the development and reduction to practice of these processes must await further advances in the technology of handling corrosive solids and gases at high temperatures, under high vacuum and possibly even under pressure'.

Calciothermic reduction of zirconium tetrafluoride

The bomb reduction of anhydrous zirconium fluoride offers yet another alternative approach to the production of ductile zirconium. The fluoride is easily prepared either by desiccating the monohydrate, ZrF_4 H_20, in a stream of dry hydrofluoric acid or by reacting zirconia with ammonium bifluoride and decomposing the double fluoride in vacuo. Fluoride has the added advantage of being much less hygroscopic than the chloride, so that the exclusion of oxygen in the extraction step is no difficult problem.

In the tests carried out at the Ames Laboratory, Iowa[15], several pounds of good quality zirconium metal have been obtained by the reduction of the tetrafluoride with calcium, in the presence of zinc and a thermal booster (like I_2). The reaction is conducted in a CaF_2 lined steel bomb and once initiated, is sufficiently exothermic to be self-sustaining. Zinc combines with zirconium formed in situ, and the dense alloy, which is immiscible with the molten slag phase, separates as a homogeneous liquid at a relatively low temperature such that there is no contamination from liner materials. The zinc is later removed from the solidified alloy by vacuum distillation at 1500°C leaving a zirconium metal sponge which may be subsequently melted to massive form. With adequate precautions in regard to the purity of the bomb charge and by proper choice of the proportion of zinc and calcium to the fluoride, it has been possible to produce, by this method, a ductile metal in a high degree of purity and in good yields.

Though the suitability of the process to large-scale production of zirconium remains to be established, it suggests, at least in principle, a simple and direct method for preparing many zirconium base alloys, with control of composition and homogeneity.

Electrolytic Zirconium

In an intensive programme for evolving a commercially acceptable continuous production scheme for zirconium, it is only natural that the electrolytic method should receive attention for reasons of simplicity and economy. While possibilities of aqueous electrolysis of zirconium solutions have been ruled out in view of the great reactivity of the finely divided metal, qualified success has been reported from the U.S. and Japan with fused salt baths which permit isolation of a coarsely granular product.

After detailed exploration of many electrolytic salt baths, variously composed of alkali and alkaline earth chlorides with additions of ZrO_2, $ZrCl_4$ and K_2ZrF_6, Horizons, Inc., Cleveland, Ohio,[16], have arrived at an optimum composition made up of 33% by weight of K_2ZrF_6 and 67% by weight of NaCl. In the development of the process to its present form, it has been established that (i) operation in an inert atmosphere with an inert crucible anode (ii) use of recrystallised salts and (iii) pre-electrolysis below decomposition voltage, are factors contributing to better quality deposits. A temperature range of 800°-850°C is recommended for obtaining a compact, carrot like deposit of zirconium crystals on the cathode.

Electrolytic deposits from the NaCl-K_2ZrF_6 bath average about 30% by weight of metal, the rest being soluble sodium and zirconium halides. The cathode deposit is crushed and pulverised and leached in water to remove the solubles. Sieve analysis of the final product shows more than 60% retention on a 100 mesh sieve and nearly 80% retention on 150-mesh.

Process development at Horiz.Inc. has reached a stage where it is possible to produce 30-40 lbs. of zirconium metal in a single run at acceptable current efficiencies and at a rate of 4-6 lbs./hour which is comparable with the Kroll process in its earliest form. The zirconium metal, after compacting and arc melting, has been found to have a BHN of 150-165 which is good enough for hot and cold working. The impurity levels are not so very objectionable either. Typical samples show an oyygen content ranging from 0.06-0.09%, with nitrogen at 0.003%, and carbon 0.02-0.06%. A recent report from the U. S. says that the Kennecott Copper Company is putting up a non-government-sponsored pilot plant for zirconium using the Horizons process.

Recent work in Japan on electrolytic zirconium has centred around $ZrCl_4$ baths. It is claimed that the crystals show a purity of 99.3% and plans are being drawn to commercialise the process.

Separation of zirconium and hafnium

Hafnium occurs in nature in invariable association with zirconium to an extent of 1 to 3%. It has properties almost identical with those of zirconium and as its atomic radius is almost the same, it goes into complete solid solution in the metal. Hafnium, however, has a high neutron capture cross-section (115 barns) and in proportions exceeding 0.02%, it drastically vitiates the otherwise attractive nuclear properties of zirconium, so that its elimination is an essential step in the reactor metallurgy of zirconium. Among the methods recommended for separation are (i) fractional crystallisation, (ii) fractional distillation, (iii) ion exchange, (iv) solvent extraction, (v) selective dechlorination of tetrachloride, and (vi) disproportionation of halides.

The Indian process of vapour-phase dechlorination aims at selective conversion of zirconium tetrachloride vapour to zirconium dioxide by reaction with controlled mixtures of chlorine and oxygen. For effectiveness of separation, however, the reaction would have to be carried out at high temperatures with gas mixtures containing very low percentages of oxygen.

The multi-stage fractional crystallisation of the fluozirconates, that has been pursued in Russia[17], is laborious but the costs might be reasonable if the process can be linked with the silicofluoride extraction of zircon and followed by the electrolysis of K_2ZrF_6.

The American process[18], described at the first Geneva conference, depends on the preferential extraction of hafnium by methyl isobutyl ketone from an acid solution containing thiocyanate. Zirconium tetrachloride containing hafnium is dissolved in hydrochloric acid and ammonium thiocyanate is added; the solution is equilibrated with methyl-isobutyl ketone in a counter current flow system whereby hafnium is transferred to the organic phase. The aqueous raffinate is diluted and treated with sulphuric acid at a pH of 1.4-1.8 between 170°-195°C when zirconium sulphate precipitates. Calcination of the sulphate or hydroxide after treatment with ammonia, gives an oxide containing $<0.02\%$ hafnium. As at present operated, the separation step contributes nearly 40 per cent to the cost of nuclear quality zirconium. The development of a cheaper and more efficient process would therefore be a great step forward.

The Commonwealth Scientific and Industrial Research Organisation, Australia, issued a patent two years back for the separation of hafnium from zirconium, by selective reduction of the zirconium halides, effected in four steps[19]: (i) Iodine is allowed to react with zirconium carbide in a Kroll-type unit and the crude zirconium iodide condensed at the top. (ii) The removable top is transferred to another similar vessel, where ZrI_4 is redistilled under vacuum and reacted with zirconium metal powder at 500°C to form ZrI_3. At the end of the reaction the volatile iodides containing all the hafnium and aluminium, and 50 to

70 per cent of the titanium are condensed at the top, leaving hafnium-free zirconium triodide, residual zirconium, iron and vanadium and some TiI_2 at the base. (iii) ZrI_3 is disproportionated at 350°C, again under vacuum, to yield pure ZrI_4 vapour and a solid residue, of ZrI_2, zirconium metal, iron and vanadium. (iv) Pure ZrI_4 vapour from step (iii) is passed through a dissociation chamber to deposit zirconium metal.

More recently, the same principle has been extended to the selective reduction of zirconium chloride according to the following scheme :—

$$3ZrCl_4(g) + Zr \leftrightharpoons 4\ ZrCl_3(s) \quad .. \quad (430°C)$$
$$2ZrCl_3(s) \leftrightharpoons ZrCl_2(s) + ZrCl_4(g) \quad (500°C)$$

The zirconium tetrachloride from the second step is very low in hafnium and can be fed to the Kroll process for producing low-hafnium sponge. The dichloride, on the other hand, is recycled as the reducing agent for the next batch :

$$ZrCl_2(s) + ZrCl_4(g) \leftrightharpoons 2\ ZrCl_3(s) \quad .. \quad (430°C)$$

It has been reported that a single reduction-disproportionation cycle gives an 80% recovery with a halfnium content of 500 ppm. Another cycle seems necessary to bring the hafnium level to 60 ppm to satisfy nuclear standards.

It is claimed that hafnium-containing zirconium sponge can be used for this selective reduction and that in a few cycles the sponge is purged of all its hafnium. In the disproportionation step, hafnium is considered to react with $ZrCl_3$ forming $ZrCl_2$ and $HfCl_4$ and the latter passes into the vapour.

$$4\ ZrCl_3 + Hf \leftrightharpoons 4\ ZrCl_2 + HfCl_4\ (g)$$

A repetition of the cycle gives a zirconium dichloride residue clean enough for subsequent reductions.

The CSIRO process has great potentialities. The use of zirconium chloride makes handling easier. The USI chemicals have already secured exclusive rights for this development and are putting it into pilot plant operation at Ashtabula.

Melting of zirconium and zirconium alloys

Zirconium metal, whether it be in the form of Kroll sponge or electrolytic powder or as iodide bar, has to be consolidated by melting (or powder-metallurgy techniques) before fabrication is possible.

The melting of zirconium (and its alloys), however, presents unusual problems. Molten zirconium is perhaps the nearest approach to the universal solvent and is extremely reactive not only towards the

common gases but also towards most of the conventional refractory materials. If the ingot is to be substantially free of contaminants so that the ductility of the metal is preserved, special melting techniques have to be adopted.

Of the several ingenious artifices suggested in order to circumvent the crucible problem, 'float melting', 'drip melting', and 'autocrucible melting' may be mentioned for their outstanding novelty. In float-melting, the metal is heated and melted without a crucible, by suspension in space within an electromagnetic field, generated by applying high frequency alternating current to two coaxial coils connected in series opposition. In drip-melting, a bar of metal is fed vertically into an induction coil so that the end melts continuously and drains into a copper mould kept below. In 'autocrucible melting', a solid piece of zirconium itself supports a top layer of molten metal; a pan-cake shaped induction coil is placed above to heat the metal by eddy-currents and more of metal is fed into the molten pool. None of these techniques has, however, been employed for obtaining large-sized zirconium ingots.

In the early stages of development work at Albany, Oregon, U. S., zirconium was melted in vacuum in graphite crucibles heated by split-graphite resistor elements. This, however, led to a carbon pick-up of 0.1—0.3% which was undesirable for applications where corrosion resistance was important. And so the more satisfactory procedure of cold-crucible arc-melting, with non-consumable as well as consumable electrodes, has been adopted.

When it came to the production of zirconium-alloy ingots by consumable electrode melting, further improvements in technique were called for, to ensure homogeneity[20]. Incorporation of the alloying constituents directly into the compacted electrodes was not so satisfactory as the low-melting metals showed a tendency to drain out of the electrode even from a height, because of the temperature gradient along the electrode. Better results have been obtained by providing for continuous alloying additions, during melting, of chopped ribbons or pressed tablets, through a metering device which is coupled to the zirconium electrode feed through a gear-system. Improved homogeneity is achieved by remelting the allow-ingots in vacuum, which also eliminates gas cavities.

The consumable electrode system permits melting at the rate of 240 lbs|hr. for 6″ dia. ingots at 0.56 kw hr|lb., and 600 lbs|hr. for 10″ dia. ingots at 0.36 kw hr|lb. Arc cast zirconium and zirconium alloy ingots are currently made in diameters from 4″ to 12″ with weights up to 1000 lbs and even more. Prior to fabrication, ingots are rough machined to remove surface defects and any small local defects still persisting are eliminated by surface-grinding. A recent innovation for the conditioning of ingots, without excessive scrap loss, is surface-fusion by shielded arc welding[21]. The ingot is rotated on

a lathe fixture inside a helium-atmosphere box and the welding bead is run over the periphery fusing the side-wall imperfections. Surface fusion has a distinct advantage over other types of conditioning as it removes the majority of sub-surface porosity.

Fabrication of zirconium[22]

With the background of experience gained in the handling of the stainless and high alloy steels and, more recently, of titanium and its alloys, the fabrication technology of zirconium has not presented any insurmountable problems. Finished mill products such as forged slabs, bars, billets, and plates, rolled sheet and strip, wire and rod forms, welded and extruded tubes are now being turned out on a commercial scale.

Zirconium has a wide hot-workability range and can be easily rolled or forged to shape. The formation of a tenacious, superficial layer of oxide is an advantage, as it prevents seizing of mating surfaces. Elaborate precautions are, however, required in extrusion and deep-drawing processes, if galling is to be avoided.

On an industrial scale, preheating of zirconium ingots can be done in conventional oil or gas fired soaking furnaces used for steel, provided care is taken to avoid direct contact with the flame. Four inch dia. ingots are generally soaked for about one hour and 12″ dia. ingots, for 2 hours, at 980°C prior to forging. It is desirable to preheat the metal to a sufficiently high temperature so that the forging or rolling sequence is completed without reheating, but this may not be possible where large reductions are intended.

The following are the forging temperatures recommended for the different grades of zirconium :—

	Starting Temp.	Finishing Temp.
Iodide Zr.	760°C	600°C
Kroll Zr.	850°C	650°C
Zircaloy-1	980°C	750°C

Forged billets and slabs are conditioned by shot blasting to remove oxide-scale, and pickling in 8 to 12% HNO_3—2 to 4% HF; local imperfections are removed by grinding.

Encasing of the conditioned ingots and billets in gas-tight steel sheaths prior to hot rolling permits operation at higher temperatures and gives a clean scrap. There is, however, a significant addition to production costs. It is more practicable to carry out the hot operations with unsheathed zirconium and if the sizes are large enough the oxide penetration is not a serious matter. The scale on hot rolled strip or

sheet is quite tenacious but is generally broken up with a sand blast, followed by an acid pickle.

Cold rolling of zirconium does not lead to any rapid work-hardening. Maximum reductions of 10% per pass, to a total of 35% between anneals, are permissible. Annealing temperatures range from 700° to 850°C.

Galling problems are particularly acute in the fabrication of zirconium rods and tubes by extrusion. Till recently, it was considered essential to adopt a 'sheathing process'. In the production of extruded tubes, the billet was first bored, then clad on the inside and outside, before carrying out normal tube extrusion. However, with increasing availability of zirconium, it has become apparent that extrusion without the metallic sheath is practicable if effective lubrication can be provided. Collodial graphite, molybdenum sulphide, and molten glass are among the lubricants recommended. Extrusion of zirconium has now developed to such a stage that even successful piercing of solid billets for tube fabrication has been reported. Hot extrusions are generally performed from 750° to 1000°C.

Zirconium shapes can be machined satisfactorily to close tolerances if the work-hardening characteristics, the galling tendency and pyrophoricity of the metal are adequately taken into account.

Though the reactivity of zirconium originally gave rise to misgivings as to its welding qualities, it has turned out that, with some precautions against atmospheric contamination, it is easier in practice to produce sound and ductile welds with zirconium than with more common materials like the aluminium alloys and a number of alloy steels. Special inert atmosphere welding chambers and inert-gas-shielded welding torches with trailing shields have been evolved to protect the weld pool and the hot metal in the rear and below, from picking up oxygen and nitrogen[23]. The low thermal expansivity of zirconium and the small volume change associated with the phase transformations permit the welding of intricate structures with a minimum of distortion. As the metal has a high solubility for its own oxides, no fluxes are needed in welding and thereby flux-entrapment is eliminated. Relative to many other commonly welded metals, zirconium requires a higher welding current, about one ampere for every mil of penetration.

Powder metallurgy of zirconium[24]

Though arc melted zirconium products are now plentifully available in large variety, powder metallurgy techniques offer certain advantages perticularly in the fabrication of unusual shapes and porous parts, and also for difficult alloy and cermet compositions. As sintering is carried out at a temperature far below melting point, there is less chance of impurity pick-up, and as further fabrication steps are cut out, there is saving of costly material.

Zirconium powder used in powder metallurgy should have a high degree of purity, a consistency in particle size and a low compression ratio. Kalish[25] has listed possible processes for preparing the powder: —(i) Reduction of zirconia with calcium, (ii) Reduction of zirconium tetrachloride with sodium, (iii) Reduction of $Na_5Zr_2F_{13}$ and K_2ZrF_6 with sodium, and (iv) Hydrogen embrittlement of massive zirconium. The last one, which is about the best, is based on the formation of a brittle hydride when chunks of Kroll or iodide zirconium are exposed to a stream of hydrogen at 800°C. Zirconium hydride is readily comminuted and decomposed in vacuum at 800°C to give the metal powder. As there is partial sintering in the vacuum-decomposition step which might lead to an irregular particle size distribution on further comminution, it is recommended that the zirconium hydride powder itself, which contains a larger percentage of fine particles, might be used for compacting and sintering in powder metallurgy operations. Reduction in processing time and cost, and operation at a lower sintering temperature at smaller compacting pressures with less chances of impurity pick-up are some of the advantages accruing from the direct use of zirconium hydride. Acid leached Kroll sponge and electrolytic zirconium are alternative sources for supplying good-quality powder.

Powder metallurgy techniques are particularly advantageous in the preparation of zirconium alloys, when the special properties desired are not otherwise obtainable or when there is a large difference in the melting points of the constituents which would render it difficult to obtain proper homogenisation. Compacting pressures for mixed alloy powders are in the range of 30-70 tons|sq. in. Sintering time and temperature would depend on the particular alloy system. The properties of dense, homogenised alloys obtained by powder metallurgical sintering processes are often similar to those of arc-melted and cast alloys. Considerable success is reported with Zr-U and Zr-Sn systems of interest in reactor engineering.

Zirconium alloys

Though superior high-temperature properties might be expected of zirconium by virtue of its high melting point, the strength of the metal drops off rather rapidly with increasing temperature and loses significance at 500°C; the allotropic transformation temperature at 862°C seems to give a truer indication of mechanical behaviour. Again, while it is generally accepted that zirconium has exceptional corrosion resistance, the commercial grade metal gives variable performance depending on its composition. Research work in recent years on alloy developments with zirconium has therefore mainly been concerned with improvement in high temperature strength[26] and extension of corrosion limits, so as to widen the range of applications. The indications are that it might eventually become possible to utilise a less expensive zirconium sponge as base material, which is higher in impurity content than at present admissible.

Useful alloying additions intended for improving the high temperature strength of zirconium may broadly be classified into 2 groups:— (i) Alpha-stabilisers or elements which stabilise the h.c.p. phase by raising the alpha-beta transition temperature and (ii) beta-stabilisers or elements which stabilise the b.c.c. phase by lowering the alpha-beta transition temperature.

The more important alloying elements belonging to the first group are aluminium and tin. While Zr-Al alloys are known to retain good mechanical strength even up to 650°C, it is unfortunate that their scaling resistance is poor, and they cannot be considered for extended use at high temperatures. The alloys with tin have shown greater promise, though their oxidation resistance at elevated-temperatures is somewhat inferior to that of pure zirconium. Zirconium-tin alloys have excellent ductility and satisfactory impact strength. Tin is also reported to contribute to a substantial increase in creep resistance at moderately high temperatures.

Among the elements which tend to stabilise the beta phase in zirconium, are chromium, cobalt, iron, manganese, moloybdenum, nickel, niobium, tantalum, thorium, titanium, tungsten, uranium and vanadium. The Zr-Mo alloys are the most promising in this group, as they have excellent room-temperature strength which is retained to a moderate degree at the higher temperatures and they are amenable to heat treatment. Alloys containing less than 5 wt. pct. molybdenum transform on air quenching to acicular alpha, and on very rapid quenching to martensite. In proportions up to 20 wt. pct., niobium and tantalum impart high temperature strength. Molybdenum and tantalum are also reported to confer beneficial effects with respect to the creep resistance of zirconium.

Tensile properties of some binary and ternary Zr alloys

	Yield strength in lbs. per sq. inch (0.2% off set)		Elongation % in one inch	
	Room Temp.	500°C	Room Temp.	500°C
3% Al. ..	55,000	28,000	20	23
3% Sn	45,000	24,000	35	40
3% Mo ..	73,000	30,000	30	40
3% Nb	73,000	30,000	30	45
3% Sn-1.5% Mo ..	59,000	30,400	25	42
3% Sn-3.3% Al .	78,900	39,400	3	6

One of the most outstanding alloys in the ternary group is Zr-4 wt. pct. Sn and 1.6 wt. pct. Mo, which is readily rolled at 800°C and has more than four times the creep strength of zirconium at 500°C. By suitable heat treatment, it is possible to produce all the three forms of zirconium with this alloy. Beta-zirconium can be retained by equilibrating the alloy between 800-900°C and quenching in water, under which conditions an alpha phase low in Mo and a beta phase

enriched in Mo are obtained. Martensite is produced by heating the alloy to 1000°C and water quenching. Cooling at a rate slower than 1,000°C|min. from the 1,000°C range would result in acicular alpha zirconium. The tensile strength of Zr-Sn-Mo in the annealed condition is about 90,000 p.s.i. and can be improved by heat treatment to more than 140,000 p.s.i. The alloy can be cold reduced more than 20% in the annealed state[27].

Corrosion resistant alloys for use in high temperature water

The reaction of zirconium with high temperature water occurs in two stages. The first stage is characterised by the formation of a thin, adhesive oxide film corresponding to passivation. In the second stage, however, a more rapid corrosion rate sets in, which is associated with the appearance of a non-adherent, white corrosion product on the surface, followed by excessive spalling. The 'break away' as this second stage is described, is dependent on the operating temperature and the impurity content of the metal. Even very low levels of nitrogen (>0.005%), carbon (>0.04%) and aluminium (>0.01%) are known to affect very seriously the corrosion resistance of zirconium to water at high temperatures. In developing zirconium alloys for use in pressurised water systems in power reactors, it has been attempted to counteract the influence of these impurities and thereby delay or totally eliminate the appearance of the spalling white oxide crust.

Exploratory investigations with binary additions of tin to zirconium and ternary and higher order additions of iron, nickel and chromium to Zr-Sn alloys have led to the evolution of the zircaloys which are increasingly being preferred to unalloyed zirconium for specialised applications. Zircaloy-2 is a sponge-zirconium base alloy containing 1.5% tin, 0.12% iron, 0.05% nickel and 0.10% chromium and is established to have about the best combination of corrosion resistance and mechanical strength, hitherto reached[28]. Zircaloy-3 (Zr-0.25% Sn-0.25% Fe), which has not been completely evaluated, is expected to permit operation at temperatures even higher than is possible with zircaloy-2. Its greater amenability to cold-working shows promise of substantial reduction in fabrication costs.

Mechanical strength of the zircaloys

	Yield strength		Ultimate strength		
	Room	500°C	Room	500°C	
Zircaloy-2 ..	43,000	19,000	64,000	33,000	lbs.|sq. in.
Zircaloy-3 ..	37,000	14,000	60,000	26,000	lbs.|sq. in.

Tin in zircaloy-2 overcomes the deleterious effects of impurities like nitrogen which are likely to get into the sponge feed stock and is reported to promote the adherence of the zirconium oxide film, though the

actual mechanism is not yet fully understood. The salutary effect of iron, nickel and chromium additions is believed to be associated with the role of hydrogen in the corrosion behaviour of zirconium; these elements are expected to promote the recombination of the nascent hydrogen produced at the surface by reaction with water and thereby limit the amount of hydrogen picked up by the metal. A significant advantage which is derived from the decreased sensitivity of zircaloy-2 to impurity content (within limits) is that the Kroll process sponge can be directly utilised without any further refinement.

Zirconium scrap

A greater utilisation of zirconium scrap is bound to bring about a favourable displacement in zirconium economics. While solid scrap, such as that available from edge trim and tailings from strip, can be compressed by admixture with Zr sponge or tack welded as such to give consumable electrodes for remelting, machining scrap needs more careful handling, to avoid any enhancing of impurity levels which would give rise to a less ductile material on remelting. The major offending contaminants are carbon (from lubricants) and oxygen from the oxide film covering the machined chips. Techniques have now been developed for removing oils (by centrifuging and washing in CCl_4 and alcohol), mechanically adhering contaminants like iron (by leaching in HCl and washing) and oxygen (by treatment with calcium vapour under controlled vacuum at 600°-675°C).

Future of zirconium

The high cost of the Kroll process is the principal impediment in the more rapid growth of the zirconium industry. The search, therefore, for an alternative process for the extraction and refining of zirconium is continuing in order to produce cheaper zirconium.

In reactor applications where high grade hafnium-free zirconium is required for reasons of neutron economy, the hafnium separation step poses special problems. As mentioned earlier, the solvent extraction process, for instance, accounts for nearly 40 per cent of the cost of zirconium. The development of a cheaper process to effect the removal of halnium is therefore of prime importance. In this context the USI sodium process coupled with the Australian process for hafnium separations seems to hold special promise.

The high cost of production with the existing processes is mainly occasioned by the many quality-control steps that are deemed essential. It is probable that with the development of new alloys, the impurity tolerances allowed in zirconium may be raised. Nevertheless, on account of the great sensitivity of the metal to impurities, it is unlikely that the metal will be as freely and cheaply available as the conventional engineering metals. It will find its major applications in nuclear reactors and in chemical plants on account of its corrosion resistance.

It has been estimated that by 1960, 30 per cent of the total zirconium production, at least in the U.S.A., will go into non-reactor uses specially in the chemical engineering industries.

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Discussions

Dr. Brahm Prakash (*A.E.E., Bombay*) : There is a brief reference in our paper to the selective reduction of zirconium tetrahalides as a means of hafnium separation which has been developed by the C.S.I.R.O. of Australia. As you know, the Chairman, Dr. T. R. Scott, comes from the same organisation. Might I therefore request him to make some additional comments if he is in a position to do so?

Dr. T. R. Scott (*C.S.I.R.O., Australia*) : The Australian C.S.I.R.O. process has additional advantages in that traces of many other impuri-

ties in the original zirconium tetrachloride are incidentally removed in the course of processing, so that the product of zirconium meets not only the purity specification for hafnium but also for all other impurities. Ferrous chloride builds up in the crucible but can be removed by distillation, in the furnace used for magnesium chloride removal, whenever too much has accumulated.

A disadvantage is the coating of zirconium metal initially with a skin of non-volatile zirconium trichloride. This slows down the reaction but can be rectified by spreading the zirconium on trays to give a large surface area. It is hoped that small modifications to the process will ultimately overcome this problem and also enable a hafnium content of 0.01 per cent to be reached in one stage.

It should also be noted that, in NaCl-K_2ZrF_6 melts, a separation factor exists during electrolysis with selective deposition of hafnium at the cathode at 850°C. Thus 90 per cent of the hafnium can be removed, leaving only 0.2% in the melt. The separation factor after this concentration has been reached is however much less. (Ref. I.E. Newnham, Waverley Gold Medal Essay, Research, November 1957).

Dr. H. N. Sinha (*I.I.T., Bombay*) : The method of hafnium separation by the selective reduction of zirconium tetrahalides, as developed by the C.S.I.R.O. of Australia, evidently has a great attraction. But in view of the fact that the disproportionation reactions result in low yields, is it not possible to eliminate the second step: $2\ ZrCl_3 \rightleftharpoons ZrCl_2 + ZrCl_4$, and directly electrolyse the zirconium trichloride produced in the first step using a suitable carrier electrolyte? Trichloride electrolysis has yielded quite encouraging results in titanium production and so may be quite successful in the production of zirconium.

Author's Reply: The electrolysis of zirconium halides is still in the development stage. I do not think that zirconium trichloride electrolysis has as yet been attempted on a commercial scale for the production of zirconium metal.

Dr. H.N. Sinha (*I.I.T., Bombay*) : I should like to mention that zirconium trichloride electrolysis has been tried with sucessful results in the laboratories of the school of Metallurgy, Melbourne University.

Mr. R. Manocha (*A.E.E., Trombay*) : I should like to ask the Chairman whether it has been possible to get down to a hafnium content of 0.01% in zirconium, in a single stage reduction by the C.S.I.R.O. process, even on a laboratory scale.

Secondly, if zirconium trichloride forms an impervious coating on the zirconium sponge powder, what was the technique adopted for exposing fresh metal surface for further reaction?

Dr. T. R.Scott (*C.S.I.R.O., Australia*) : I can only say that condi-

tions are ideal on a laboratory scale for single stage elimination of hafnium. The C.S.I.R.O. process is now being studied on pilot plants at the National Distillers Corporation. Further information is not available.

Mr. C. V. Sundaram (*A.E.E. Trombay*) : Is it true that it has not been possible to go beyond an enrichment of 30% hafnium in the volatiles, in the first step: $Zr + 3ZrCl_4 \rightarrow 4ZrCl_3$? If so, would this argue against the efficiency of the C.S.I.R.O. process?

Dr. T. R. Scott (*C.S.I.R.O., Australia*) : An enrichment to 30% hafnium is adequate for further treatment towards isolation of pure hafnium salts.

PRESENT STATUS OF BERYLLIUM METALLURGY

*By T. Banerjee and P. B. Chakravarti**

The metal beryllium was a chemist's "curiosity" even at the beginning of the present century. It was in fact heretofore considered as a "rare metal" and of little practical use. But investigations, made in Germany and America in the early part of this century, showed it to be a promising metal. Binary and ternary alloys of beryllium with some non-ferrous metals like magnesium, aluminium, nickel, cobalt and particularly those with copper are unique in some of their physical properties and are industrially very useful. In fact, it is claimed that "beryllium is to copper what carbon is to iron". Beryllium oxide is an important material for special types of refractory wares. Because of its extra-ordinary resistance to thermal shocks and high electrical resistance even at high temperature, it may rightly be called a "super-refractory" which may be used with great advantage for making special types of crucibles, muffles, electric furnace linings, laboratory boats and vacuum tubes. But two recent discoveries, which are considered primarily responsible for its meteoric rise to importance during World War II relate to its use in the nuclear energy field. One is about its use as a source of neutrons when bombarded with α - particles while the other and the most spectacular is that the metal is one of the best moderators and reflectors for atomic reactors.

Because of its strategic importance, particular attention is being focussed on the metallurgy of this metal in several countries. India, being one of the major beryl producing countries is naturally interested in it. Considerable work has been done at the National Metallurgical Laboratory on the processing of beryl. Recent development in the metallurgy of this metal is presented in the following pages.

Occurrence of beryllium ores

Beryllium is widely distributed in nature but in very minute quantities. It forms 0.001% of igneous rocks according to Washington[1] and 0.0006% according to Goldschmidt[2]. Recent determination of beryllium content in the earths crust by Rankama & Sahama[3] confirms the results of Goldschmidt. According to them, beryllium constitutes about 6 parts/million (i.e., 0.0006%) of igneous rocks and 3.5 parts/million (i.e., 0.00035%) of shales. It is 32nd in abundance among the elements of earths crust and approximately of the same rank, as caesium, scandium and arsenic. Though there are nearly thirty minerals in nature containing beryllium, its only commercial ore is beryl, which is chemically beryllium aluminium silicate containing 14.1% BeO (or

* Of National Metallurgical Laboratory, Jamshedpur.

5% Be). Other important minerals rich in beryllium are helvite (13.5% BeO), phenacite (45.5% BeO) and chrysoberyl (19.7% BeO). Their occurrences in nature are very limited and can by no means be considered to be useful. Beryllium minerals are mostly found in pegmatites, granites and syenites, though non-pegmatitic beryllium containing deposits have also been discovered. Even sometime back beryl was not mined for its own sake. It was always obtained as a by-product from feldspar and mica mining operations and only those crystals were recovered which were large enough to be hand sorted. But the picture has changed now. The metal has been found to be very useful in nuclear power industry. Because of this, enhanced interest in the supply of raw material for this metal is being shown everywhere and steps are being taken to develop new technique for utilising low grade ores.

The principal producers of beryl ore are the Union of South Africa, Southern Rhodesia, Brazil and India. Small amounts are also produced in British East Africa, French Morocco, Mozambique, Portugal and Canada. In the United States, principal sources are located in Colorado, Maine, New Hampshire and South Dakota.

Occurrence in India[1]

Pegmatitic deposits of beryl occur in many parts of India, particularly in Rajputana, Bihar and Madras. Most productive deposits are located in Ajmer Merwara and Mewar, where crystals of very large sizes are obtainable, some measuring 4 ft. across and upto 20 ft. in length and yielding as much as 20 tons of beryl. Beryl of gem quality is also found there. Presence of beryl and aquamarine has been detected in the pegmatites of Kashmir along with some other minerals like muscovite, tourmaline and garnet.

The mica bearing pegmatites of Hazaribagh district in Bihar contain beryl. The mineral is recovered as a by-product by hand picking from mica mining operations in Kodarma forest. The mineral has also been found in Monghyr district.

Mica bearing pegmatites of Nellore district in Andhra Pradesh and pegmatites of Coimbatore district in Madras also contain beryl. But as the quantities recoverable are very small, no serious attempt has till now been made to develop the mines for recovery of beryl.

Pegmatites and granites occupy very large tracts in Hyderabad, Madhya Pradesh, Orissa & Assam and also in some other provinces. It is considered very likely that with proper Geological Mapping & Exploration of these tracts, new sources of beryl will be discovered.

At present, almost all of the beryl that is produced in India comes from the mines of Rajputana. Contributions from areas of Kashmir, Bihar, Nellore, etc., are negligible. For lack of proper encouragement,

mines at those places have not yet fully developed. But the situation may soon change. Under the Second Five Year Plan, ambitious programmes have been drawn up for development of atomic power and also non-ferrous alloys for which considerable quantities of beryllium oxide and metallic beryllium would be required. Steps must be taken not only to prospect for new deposits of beryl but also to beneficiate low grade ores, now discarded. In this connexion it would be of interest to know that considerable advance has been made, particularly in America, in the processes[5] for concentrating low grade ores, though they have not reached a stage fit for commercial exploitation. For establishment of a new industry, accurate estimate of the raw materials available and assessment of the demand, actual and potential, of the finished product are essential pre-requisites. Effort should also be made to popularise beryllium alloys for use in scientific instruments and for engineering purposes.

Metallurgy

The extraction of beryllium from beryl is extremely difficult which has been taxing the ingenuity of chemists and metallurgists. Inspite of the intensive effort directed at finding out cheap and easy methods of extraction, its cost is still very high. This has naturally curbed its wide use for engineering purposes, inspite of its highly beneficial effect as an alloying element in some non-ferrous metals. There are, in commercial operation today two entirely different methods of extracting beryllium from the ore. Both involve high temperature treatment of the ore with fluxes and extraction of beryllium as a soluble salt by leaching with water. One process uses the sulphate as the vehicle and other the fluoride. In the sulphate process, separation of aluminium and beryllium is effected by way of alum formation whereas in the other process, advantage is taken of insolubility of the complex aluminium fluoride salt and high solubility of the corresponding beryllium salt.

The fluoride extraction of beryllium from beryl

The method essentially consists in mixing finely ground beryl ore with an alkali silico-fluoride and sintering the mixture at a controlled temperature. The sintered mass is again finely ground and leached with water whereby beryllium goes into solution as a soluble salt, silica, alumina, iron, etc. remaining behind as an insoluble mass. The leach liquor containing beryllium is then purified and treated with calculated amount of caustic alkali when beryllium hydroxide is precipitated. The precipitate on washing, drying and calcination gives the oxide. The entire process is schematically shown in Fig 1[6].

Sulphuric acid extraction of beryllium from beryl

This method is worked by the Brush Beryllium Co. of U.S.A. the flow sheet of which is shown in Fig. II[7].

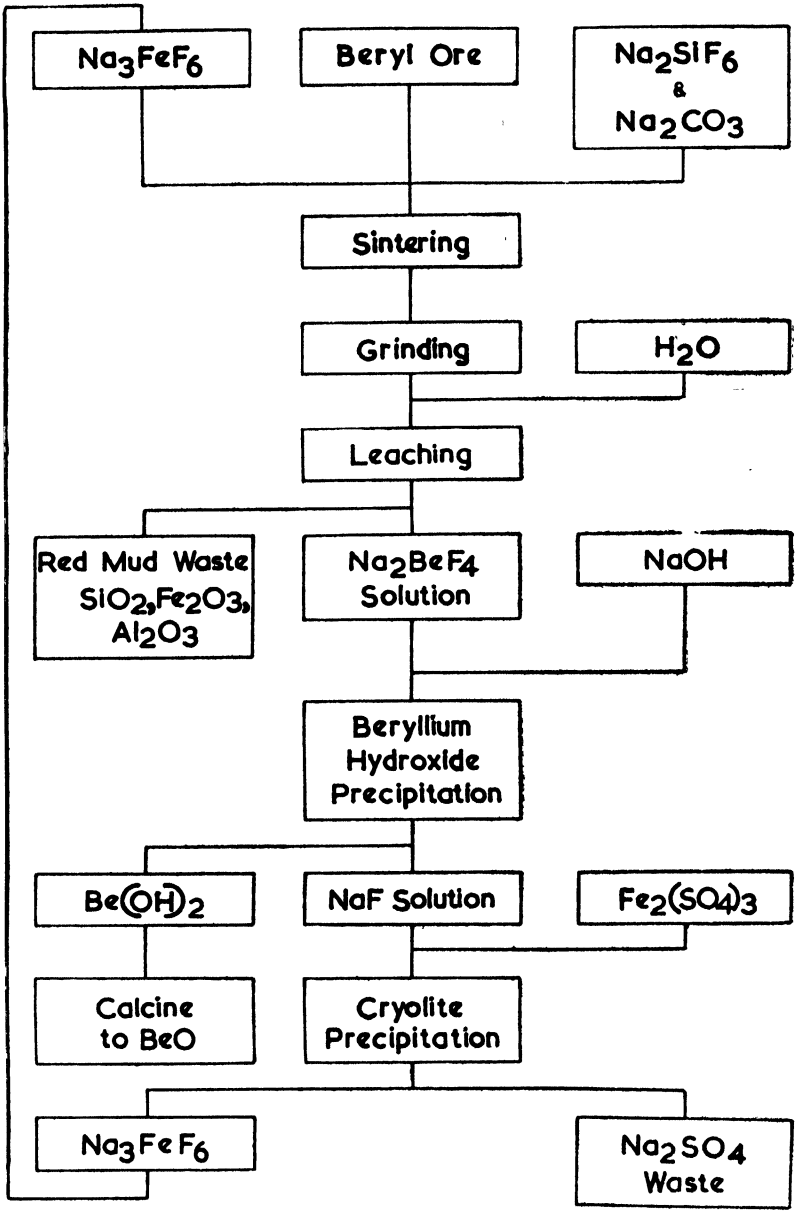

Fig. No. I—Flow Sheet of Fluoride Process for Reduction of Beryl.

The process briefly runs thus : Beryl is melted down in a carbon lined electric furnace. Molten beryl is then rapidly cooled in a stream of water. Rapid cooling is essential for a good recovery, as it makes the frit highly reactive with sulphuric acid. The frit is then dried

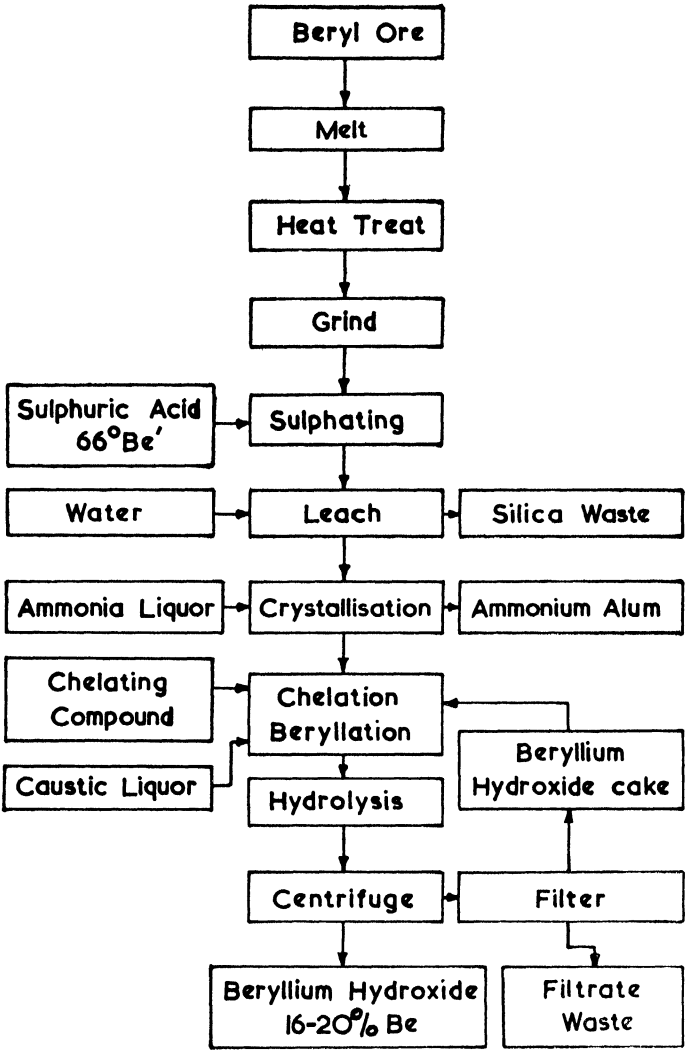

Fig. No. II—Beryllium Hydroxide Production Brush Process.

and finely ground to -200 mesh. The fine powder is then digested with sulphuric acid of 93% strength when beryllium, aluminium, iron, etc. form sulphates leaving behind a residue of silica. On leaching with water, a liquor is obtained from which 75% of the aluminium content is removed as ammonium alum. To the filtrate is next added a chelating compound, like ethylene diamine tetracetic acid, followed by caustic alkali solution. The chelating compound prevents the impurities from contaminating the beryllium hydroxide produced by hydrolysis of the sodium beryllate solution at its boiling point. On centrifuging a beryllium hydroxide cake is obtained containing 16-20%

beryllium. This cake may be used for production of beryllium fluoride for metallo-thermic reduction by magnesium to the metal or for direct production of beryllium copper alloys in an arc furnace.

America is at present the chief producer of beryllium and beryllium alloys and employs both the fluoride and sulphate processes. Choice of the process is primarily decided by the quality of the raw materials available and nature of the end products desired. The sulphate process is capable of giving a final product of very high purity. This may be desirable where a very high purity is a necessity such as for use in atomic reactors. But, ordinarily such high purity is not required. Moreover, only high grade beryl can be profitably treated this way. Treatment of low-grade ore will entail heavy loss of acid. A temperature of the order of 1500°-1600°C is also required, not always easy of attainment. Equipments to be used must also be of such materials as will resist acid corrosion.

The fluoride process definitely possesses some advantages over the sulphuric acid process in this respect. Temperature range required is of the order of 700°-800°C. The solutions are non-corrosive and hence equipment made of iron and wood would serve very well. The most distinct advantage is that very low grade is amenable to treatment by this process as only beryllium oxide constituent of the ore is preferentially attacked by the flux to the exclusion of the other constituents, unlike the acid process, where all constituents of the ore except silica are dissolved by the acid.

Work at the National Metallurgical Laboratory on the extraction of beryllium oxide from beryl

Considerable work has been done at the National Metallurgical Laboratory on the extraction of beryllium oxide from beryl. As beryllium oxide forms the starting material for metallic beryllium as well as for beryllium-copper alloys, its extraction from beryl was taken up first. Fluoride extraction method[8] was chosen for trial on semi-pilot plant basis. The flowsheet of the process is shown in Fig. III. On the average, an extraction of 80-85% of beryllium oxide from beryl was obtained with purity of the product ranging from 95 to 98%. Based on this investigation, a pilot plant scheme for production of 2400 lbs of beryllium oxide from beryl by the fluoride method was later drawn up. The calculated cost of production on a three shift basis worked out Rs. 24|- per lb of beryllium oxide which is comparable with prices prevailing abroad.

Another electrolytic process[9] has also been developed at the National Metallurgical Laboratory, the flow-sheet of which is also shown in Fig. III alongside that for the fluoride process. The process has been patented in India, U.K., France, and U.S.A.[10] It consists in electrolysing a solution of sodium beryllium fluoride in a diaphragm cell whereby a slurry of beryllium hydroxide is formed in the cathode

chamber. The slurry, after filtration and washing gives beryllium oxide on calcination. High current efficiency has generally been obtained for the process. The purity of the product obtained is of the same order as that obtained by the chemical process. That electrolysis is carried out at the room temperature is also an added advantage for the method.

As the method was not tried on pilot plant scale, it is not possible to work out its economics. But an approximate idea can be formed from a comparative study of the electrolytic and chemical processes (Fig. III). From the flow-sheet it is found that steps upto the production of a solution of sodium beryllium fluoride from beryl are common to both the processes. Again steps, beginning from the preparation of pure beryllium hydroxide upto its calcination to the final product are also common. Assuming that capital and working expenditures be more or less same for the above-mentioned steps, then the difference in capital and working expenditure for the intermediate steps will determine the superiority of one over the other.

From data obtained in course of operating these two processes, some figures, which are of course, tentative, were arrived at. The cost of electric power and chemicals comes to 14 annas per lb of oxide for the electrolytic process whereas chemicals alone would cost Rs. 6½ per lb of oxide by the chemical process. This wide difference is, however, only apparent and would, in all probability, considerably narrow down in operation on bigger scale when other factors like, capital and working expenditures for the whole processes, depreciation, cost of by-products obtained, purity of the end products, etc. are taken into consideration. It is, however, felt that there is sufficient margin of advantage left for the electrolytic process over the chemical one to warrant its adoption for industrial operation. On point of the purity of the product too, the electrolytic process is expected to give a product of higher purity than the other. The reason is that, in the chemical method, treatment with various chemicals in large amount is necessary, whereby impurities are introduced in small quantities at every step, whereas in the electrolytic process, no such possibility exists, provided materials, not attached by fluoride solution are used for construction of the equipments necessary for preparing pure aqueous solution of sodium beryllium fluoride and also for electrolysis. Also on points of ease and neatness of operation, the electrolytic process seems to be preferable.

Production of Metallic Beryllium

The production of metallic beryllium and its alloys is one of the most difficult tasks in metallurgy. These difficulties arise primarily from the very reactive nature of the metal and its compounds.

Since pioneering work of Stock and Goldschmidt[11] on the production of massive beryllium by high temperature fusion electrolysis, consi-

FLOW-SHEET FOR THE FLUORIDE PROCESS FOR BERYLLIUM OXIDE.

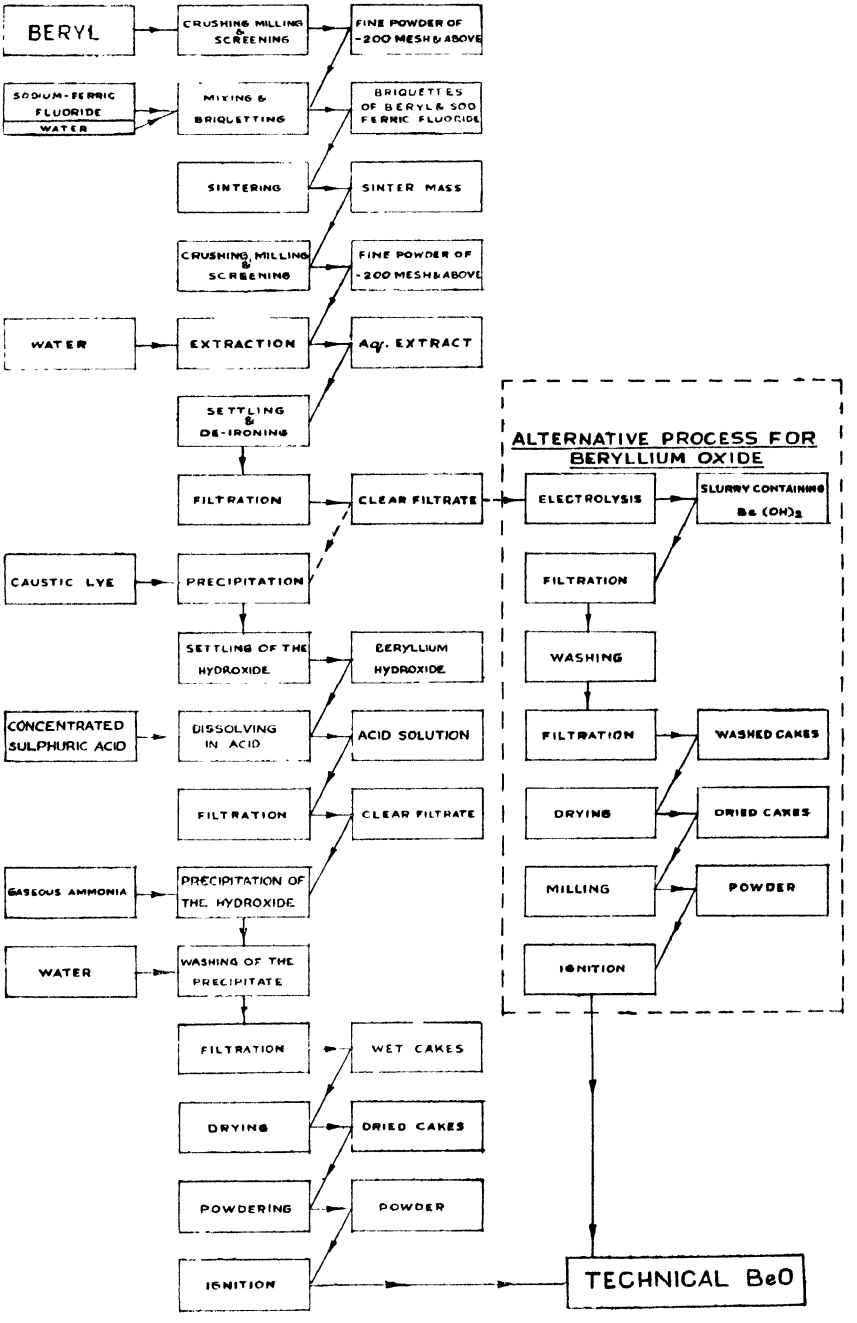

Fig. No. III

derable effort has been directed towards finding out other easier methods of making beryllium. An excellent review of all the methods so far suggested and which are considered to have commercial possibility is given by Kroll[12] in an U.S. Bureau of Mines publication.

The methods for producing metallic beryllium can be broadly divided into the following classes :

(i) Metallo-thermic reduction methods.

(ii) Electrolytic reduction methods.

(iii) Dissociation methods.

(i) *Metallo-thermic reduction methods* : (a) *Reduction of oxide* : The possibility of reducing beryllium oxide to metallic beryllium using titanium metal as the reductant was first showned by Kroll[13]. The reduction was carried out in a high vacuum and at a temperature (1400°C) above the melting point of the metal so that massive beryllium could be obtained. But if too high a temperature was used, there was contamination of the product with titanium monoxide by volatilisation. Magel[14] on the otherhand, used metallic zirconium as the reductant and a temperature as high as 1725°C. As no volatile oxide of zirconium was formed at the operating temperature he could obtain a purer product. The reduction of the oxide with calcium, magnesium, aluminium or silicon is not practicable proposition, though alloys with nickel, iron and cobalt can be obtained this way. Carbon reduces beryllium oxide at 1800°C to carbide only.

(b) *Reduction of the chloride* : The free energy-temperature diagram[15] shows that it is possible to reduce beryllium chloride with alkali and alkaline earth metals like lithium, sodium, potassium, calcium and magnesium. Wohler[16] tried potassium while Hunter and Jones[17] used sodium as reductants. Their experiments were of theoretical interest only as both the recovery and purity of the product were low. Tien[18] reported some experiments on the sodium vapour reduction of beryllium chloride. He obtained 91% yield of the metal whose purity was 96%. It is understood that this method was given large scale trials by Brush Beryllium Co. of America. Both calcium and magnesium again can be used for reduction. The disadvantage with calcium is that it is costly metal and its reaction with the chloride is violent. The case of magnesium has been discussed thoroughly by Kroll[12], who considers it to be a promising material for this purpose. Magnesium chloride, produced in the reaction, can be driven off under vacuum at 900°C after which temperature can be raised to obtain massive beryllium. Metallo-thermic reduction is generally very rapid and can be pushed to completion with an excess of the reagent. The disadvantages are that chloride being hygroscopic readily hydrolyses and lowers thereby the efficiency of reduction and secondly, due to the extreme rapidity with which the reaction proceeds, the metal is gene-

rally obtained in fine powdery form, very difficult to separate from the slag. Moreover, due to extreme fineness in size, it tends to pass into colloidal form when washed in water which is also likely to attack it.

(c) *Reduction of the Fluoride* : Study of the free energy-temperature diagram[16] also reveals that beryllium fluoride like the chloride is also reducible by alkali and alkaline earth metals. Use of sodium and potassium has not been very successful as after the reaction has proceeded to some length a stable product 2NaF, BeF_2 is formed which is not further reduced by sodium. Kroll[19] first suggested the use of magnesium and lithium for reduction. Losano[20] prepared high purity metallic beryllium using magnesium as the reductant and adding zinc for damping the reaction. The residual zinc was subsequently removed by high temperature distillation. The magnesium reduction process has been adopted and operated by the Brush Beryllium Co.[21] of U.S.A. for commercial production of beryllium which on the average assays 97% metal. The S.A.P.P.I. process[22] of Italy which was worked during the last war used magnesium for reduction of beryllium fluoride to produce beryllium-copper and beryllium-alluminium master alloys.

(ii) *Electrolytic Reduction Methods* : (a) *Fusion electrolysis of the fluoride*: Prior to the adoption of magnesium reduction method for beryllium, electrolytic methods produced most of the metal. Lebeau[23] was the first to obtain beryllium electrolytically. He electrolysed fused sodium beryllium double fluoride in a nickel crucible. Since then considerable work has been done on fusion electrolysis of the fluoride whereby the method has now reached a stage of high degree of perfection and very pure metal can be obtained. In this connexion work of Hopkins & Meyer[24], Engle & Hopkins[25], Vivian[26], Sloman[27], Illig[28] deserve mention. The procedure evolved by all these workers are fundamentally the same, though they differ in details. The fluoride compound of beryllium is electrolysed with or without addition of fluoride of alkali or alkaline earth metals, at a temperature above the melting point of the metal, whereby a dense and compact metal is obtained. This is a distinct advantage over other processes which give the metal in powdery form and requires melting in vacuum before casting and fabrication. The method however has been abandoned because of the toxicity of the waste gases and necessity of condensing the fumes to reclaim beryllium fluoride.

It has been often suggested that like alumina, beryllia[29] might also be reduced electrolytically in molten cryolite bath. The method is workable but only for low grade aluminium-beryllium alloys. The method is unsuitable for production of metallic beryllium.

(b) *Fusion electrolysis of the chloride* : Most of the metallic beryllium that was produced during the World War II, in Germany and America was by the fusion electrolysis of the anhydrous chloride. A good account of the exact procedure followed in Germany during the

War can be obtained from two reports[29] published from H. M. Stationery Office, London. Windecker[30] has also described the process thoroughly. There are two variations of the method. One is called "high temperature electrolysis" and the other "low temperature electrolysis". In the first one, electrolysis is carried out at a temperature of 760°-790°C with a bath consisting of 13-15% beryllium chloride with a balance of equal parts of sodium and potassium chlorides. The container is a nickel crucible which also serves as the cathode while a graphite rod centrally placed is the anode. The low temperature electrolysis differs from the other only in temperature and bath composition. It operates at a temperature of 370°C with a bath consisting of a mixture of equal parts of beryllium and sodium chlorides. The novelty of this process is the temperature which is not only below the melting point of the metal but also below the temperature at which rapid surface oxidation takes place. The successful operation of the process depends upon :

(a) Preparation of beryllium chloride free from oxide and moisture.
(b) The efficient disposal of chlorine
(c) Prevention of entry of air inside the cell during operation.

(iii) *Dissociation Methods*: Dissociation methods have been often proposed for making metallic beryllium. Beryllium oxide when reduced with carbon at 1800°C gives the carbide which may be dissociated at a still higher temperature, into metallic beryllium. A number of patents refer to this method of making beryllium. Kroll[31], however, is of opinion that such a method even if theoretically possible, would present a formidable task in practice.

The dissociation of a halide to produce the metal by the 'hot wire' technique of van Arkel and de Boer, which has been so successfully used for titanium and zirconum was also tried by Sloman[28] in case of beryllium. But it was a failure as the compound beryllium iodide, attacks glass and has too high a dissociation temperature.

A number of beryllium alloys can also be used for thermal dissociation in a vacuum. Zinc[32] and silver beryllium alloys would be most suitable for this purpose.

Beryllium has also been deposited by thermal dissociation of organo-beryllium compound, like diethyl beryllium[33]. But the method is of theoretical interest only as an organo-beryllium compound is very difficult to prepare and requires to be handled in complete absence of air and moisture.

Production of Beryllium Alloys

Most of the methods described above can, with slight modifications be adopted for production of beryllium alloys. Except beryllium-

copper alloy which is made by carbon reduction of the oxide, addition of metallic beryllium to produce the alloy is the usual procedure. Metallo-thermic reduction of beryllium oxide with calcium in presence of iron powder gives beryllium iron alloy[34]. Beryllium-copper alloy can also be made by this method. Metallo-thermic reduction of the chloride and the fluoride by alkali or alkaline earth metals also gives the alloys. Thus, as described before, S.A.P.P.I. produced beryllium-copper and beryllium-aluminium master alloys by reduction of beryllium fluoride with magnesium in presence of copper and aluminium respectively. Possibility has been shown to exist for the production of silver, aluminium, iron and silicon alloys of beryllium by reduction of the chloride. Fusion electrolysis with metal cathode has also been resorted to for obtaining alloys. For this purpose, fluoride and chloride dissolved in inert fluxes have been used as the baths. Thus beryllium-copper alloy has been made in the Stock-Goldschmidt process by using a molten copper cathode[35]. Low grade aluminium alloy can be obtained by using this metal as the cathode in fusion electrolysis of the chloride bath. But none of these methods has found any commercial use uptil now. It is easier and cheaper to producer copper and nickel alloys in an electric arc furnace.

Uses

Beryllium Metal : It is a light stable metal with a high melting point. Its density is 1.85 which is higher than that of magnesium but lower than that of aluminium and it has a high modulus of elasticity. Its electrical conductivity is between 40 to 45% that of copper. All these properties make it ideally suited for some special applications. Because of its low density and higher modulus of elesticity, the velocity of sound in it far exceeds that in other materials which permit of its applications in accoustics. Its atomic number is low, so is its absorption; it is 17 times more penetrable to X-rays than aluminium. This, coupled with its high melting point, makes the metal a very suitable material for windows in X-ray tubes. X-rays of longer wave length and greater intensity can be obtained which are useful for metal diffraction studies, thickness gauging, chemical analysis and X-ray therapy.

Beryllium is also used on small scale in radium-or polonium—beryllium—neutron sources. It is an efficient producer of neutrons when bombarded with alpha particles. It is also used in cyclotron for somewhat similar purpose. Thin foils of beryllium have been used as windows in Geiger counters, scintillation counters and similar other devices.

Special powder metallurgical techniques have been recently developed for fabrication of structural parts from metallic beryllium which, because of its "cold shortness", found no application so far in industry. This has opened up new fields of use for metallic beryllium

as a material of construction where its unique properties offer many advantages to the designer and engineer.

But by far the largest and the most important use in pure form is in the field of nuclear power development. Its extremely low neutron absorption cross section ($\frac{1}{2}$ that of zirconium) and its ability to moderate the velocity of fast neutrons produced in fission as well as to prevent their leakage makes it highly suitable for use in some special types of reactors[36].

Beryllium oxide : Beryllium oxide has a high melting point, low density and an extra-ordinary resistance to sudden and repeated thermal shocks. It also retains high electrical resistivity even at high temperatures. It may therefore be rightly called "a super-refractory" which can be used as refractory supports in electric unit, heater radiation shields around graphite crucibles, linings in coreless induction furnaces, cathode heating elements in radio tubes and ceramic coatings on lamp filaments. It may also be used as a component in special glass composition where high index, high dispersion and low diffraction and high permeability to ultra violet light are desired.

Beryllium oxide was at one time used in substantial quantities as a component in "Phosphor" compositions for fluorescent lamps. But it is no longer in use now because of its highly toxic and poisonous charactor.

Nuclear properties of beryllium oxide are almost similar to those of metallic beryllium. As its production in quantity with a high degree of purity is relatively easier than that of the metal, engineers visualise a bright future for it in the nuclear energy field.

The principal use of beryllium oxide is, however, for the production of commercial beryllium copper master alloy containing 4% beryllium. It is in this field where the bulk of the oxide produced, is consumed. The other fields described before, account only for a small fraction. The alloy is produced by carbon reduction of the oxide in presence of metallic copper.

Beryllium Alloys

Beryllium copper : Beryllium added as an alloying element to copper produces precipitation hardening. Nickel, iron, certain "steels", zinc and some other metals will also react in a similar manner to this additive, though these alloys for some reasons have not been commercially important.

The most important among all beryllium alloys is beryllium copper. This is in fact, the main outlet for beryllium and the mainstay of the beryllium industry as will be evident from the following Table[37].

Table I

Form in which used	*Present*
Raw ore in ceramics	3.8%
Beryllium metal	1.0%
High purity beryllium oxide	3.7%
Regular quality beryllium oxide	2.5%
Beryllium copper	88.3%
Beryllium aluminium	0.6%
Beryllium chemicals & compounds	0.1%
	100.0

During the last war, beryllium copper alloys were largely used, specially in aircraft where is said that, as many as 1500 separate beryllium-copper parts were installed in a single bomber. The following Table shows the percentage distribution of the alloy in military use[37].

Table II

Aircraft	50%
Radio & Radar	15%
Navy	15%
Army	12%
Research	5%
Miscellaneous	3%
	100

The exigencies of war virtually monopolised the use of the alloy for military purpose only. But with the cessation of hostilities, military demand sharply fell down. Consequently commercial uses of the alloy for civilian purposes were found out. In the following Table[37] will be found the industries that are customers of this alloy and the extent to which they require this alloy.

Table III

Electronics & communications	20%
Electrical manufacturing	16%
Business machines	14%
Refrigeration & air conditioning	10%
Foundries	8%
Automotive	8%
Welding	6%
Aluminium industry	5%
Non-sparking tools	5%
Miscellaneous	8%
	100

Beryllium nickel alloys: This group of alloys possess excellent strength and hardness. They closely resemble the stainless steels with respect to density and resistance to corrosion and compare favourably with high strength alloy steels so far as strength, hardness and elastic modulus are concerned. They are castable and instrument springs, hypodermic needles and surgical instruments can be fabricated out of beryllium nickel alloys. Precision castings of beryllium nickel are in use in aircraft, machine components etc.

Beryllium steels: Binary beryllium-iron alloys are coarse grained. Addition of nickel refines the grain and improves the alloy considerably, 'Nivarox' an iron—nickel—beryllium alloy with 8% tungsten, is extensively used for watch springs in Switzerland. Another steel "Beryllium contracid" is used for surgical instruments, corrosion—resisting springs and similar applications. Ticonium is used in the dental field while Elgiloy, for springs of watches, fountain pen nibs, flapper valves, surgical and dental equipment and camera parts.

Beryllium zinc alloys: These alloys are being developed by the General Electric Research Laboratories. Zinc-beryllium alloy containing 2 to 2.5% Cu is said to be superior in corrosion resistance to any other zinc alloy. This alloy may eventually replace brass in the fabrication of lamp and fuse sockets, bases and hardware.

Beryllium magnesium and beryllium aluminium alloys: Beryllium added in minute quantity to magnesium or magnesium aluminium alloys modifies their behaviour in a striking way. Even as small as 0.005% of beryllium in magnesium greatly reduces its inflammability and lessens its oxidation at the melting point. Beryllium added to aluminium alloys in quantities from 0.1 to 0.5% makes the casting of the alloys easy. It refines the grain and contributes to thermal stability. For intricate castings, it is helpful when present in the amount of 0.2% by promoting fludity of the alloy. During the last war, this alloy was used in Germany in appreciable quantity for casting cylinder heads of air cooled airplane engines.

Miscellaneous beryllium alloys: Though beryllium alloys of silver, gold, platinum and some other metals have been prepared, they are as yet of academic interest only. No commercial use for them has yet been developed.

Health Hazards[18]

It has been recognised that beryllium is a highly toxic material and constitutes a great danger to the health of workers. It is capable of producing a variety of diseases in human beings, affecting mainly, the respiratory tract, lungs and skin. These diseases may be produced either by inhalation of fine dust or mist of beryllium and its compounds or by actual contact with them. Though its toxicity far exceeds that of any other material known in chemical industry, enough in-

formation is, however, now available to make its processing quite harmless and free from any hazard. The basic principle of control is to keep down the concentration of beryllium in the air to the minimum and to prevent workers from coming in actual skin contact with beryllium containing materials. By adopting these and certain other preventive and precautionary measures, the danger of incidence of these acute diseases from beryllium poisoning among the working personnel can be eliminated.

Acknowledgement

Our best thanks are due to Dr. B. R. Nijhawan, Director, National Metallurgical Laboratory for his kind interest and helpful suggestion.

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Discussions

Dr. G. S. Tendolkar, (*Atomic Energy Establishment*) : 'The calculated cost of production on three shift basis worked out to Rs. 24|- per lb. of beryllium oxide which is comparable with prices prevailing abroad". I would like to know the break-up of this figure and how it was arrived at.

Author's reply : We arrived at this figure for per unit cost of production at the time when we prepared in 1951 a scheme for production of 2400 lbs. of beryllium oxide per annum on a single shift basis. The break up of the figures for various items of expenditure from which per unit cost production was calculated is given below :—

(1) Capital expenditure including building and its servicing, epuipment and intsallation and ventillation services	Rs.	1,81,000
(2) Contingency expenditure including supervision and labour cost, raw materials and chemicals, water, gas, electricity, maintenance and unforseen charges, for three shifts	,,	1,53,553
(3) Depreciation at 10% on the capital	,,	18,100

Hence for 7200 lbs. of beryllium oxide, total cost of production works out as follows :—

Recurring expenditure	Rs.	1,53,553
Depreciation	,,	18,100
	Rs.	1,71,653
Hence the cost of production/lb.	Rs.	1,71,653

$$\frac{1,71,653}{7200} = \text{Rs. } 24 \text{ (rounded up)}$$

RECENT DEVELOPMENTS IN BERYLLIUM METALLURGY

*By C. W. Schwenzfeier jr.**

On November 18, 1957, the Brush Beryllium Company dedicated its new pure beryllium manufacturing plant at Elmore, Ohio. This $4,500,000 construction project afforded an excellent opportunity for application of many of the advanced engineering ideas of the Brush Beryllium's 115 man staff of technicians, scientists, and engineers.

It has been a long time aim of Brush to make its process continuous and as fully automtic and instrument controlled as possible. Continuous processing generally permits use of much smaller process equipment, with attendant reduction in plant cost. Automatic instrument controlled operation, "automation," is much more reliable than human control and, more important, is capable of infinitely faster response to changes in process variables. This latter advantage of automation makes possible many processes that would be otherwise impossible.

Beryllium Hydroxide Production

The Brush process (Fig. 1) starts with non-flux fusion of beryl, $3BeO.Al_2O_3.6SiO_2$. The ore (melting point—1650°C (3000°F) is fused in a carbon lined, three phase, electric furnace (Fig. 2). Molten beryl ore is a good conductor of electricity, and it is therefore possible to operate the furnace as a resistance furnace by immersing the electrodes in the pool of molten beryl and adding raw charge to build up the furnace bath. This is a batch operation, and after the batch has been melted, the molten ore is poured through a high velocity water jet into a water-quench tank. A small amount of molten ore is left in the furnace to provide the necessary resistance to start the melting of the next batch.

Rapid quenching of the ore is essential to obtain a high extraction yield. Particles of frit larger than approximately ½ inch cool slowly enough at their cores to permit recrystallization of beryl, and these larger particles are, therefore, non-reactive with sulfuric acid. The quenched frit is screened to separate the large pieces, which are recycled to the melting furnace.

Reaction of the quenched frit with sulfuric acid will yield only 50 to 60 per cent of the contained beryllium, and therefore, an additional ore treatment procedure is required. The non-reactive beryllium oxide content of the quenched frit appears to be present in solid solution in the silica. By heat treating the frit, this additional BeO can be caused to precipitate out of solid solution, whereupon reaction with concen-

* Of The Brush Beryllium Co., U. S. A.

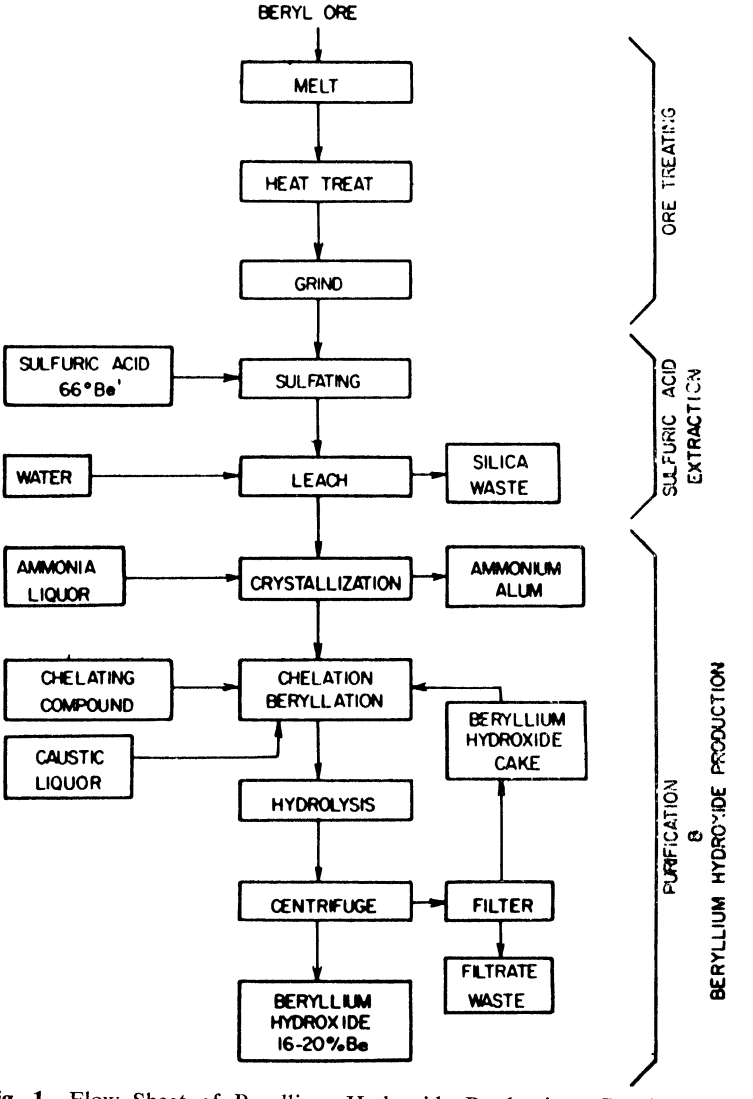

Fig. 1—Flow Sheet of Beryllium Hydroxide Production: Brush Process

trated sulfuric acid at 250°-300°C (485°-575°F) will yield from 90 to 95 per cent of the beryllium content of the ore. The precipitation of BeO from the silica takes place very rapidly, and at moderate temperatures. This equipment used for the heat treatment is a gas-fired rotary kiln (Fig. 3).

After heat treatment, the frit is prepared for reaction with sulfuric acid by dry grinding to -200 mesh. Grinding is done dry, so as to

prevent dilution of the concentrated sulfuric acid used in subsequent operations. An integral part of the grinding circuit is a pneumatic classifier, which automatically and continuously takes off the -200 mesh

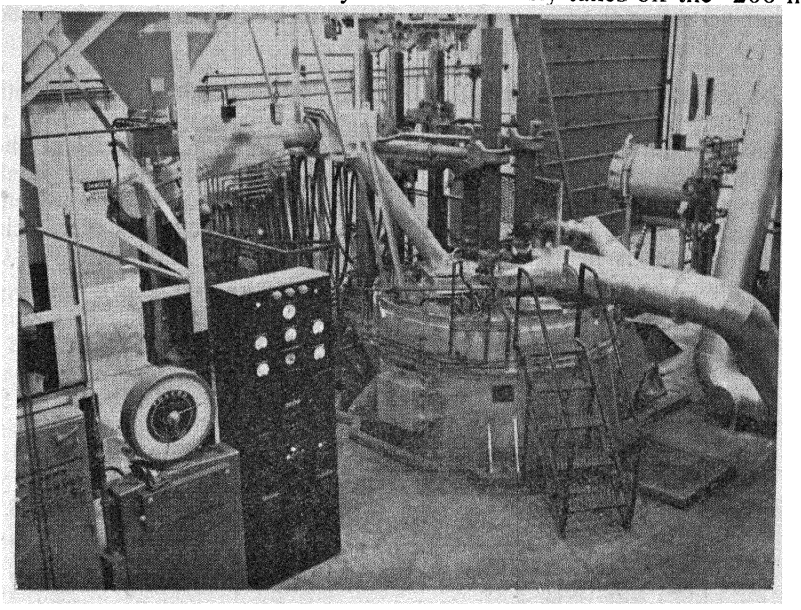

Fig. 2—1500 KW 3 Phase Ore Melting Furnace

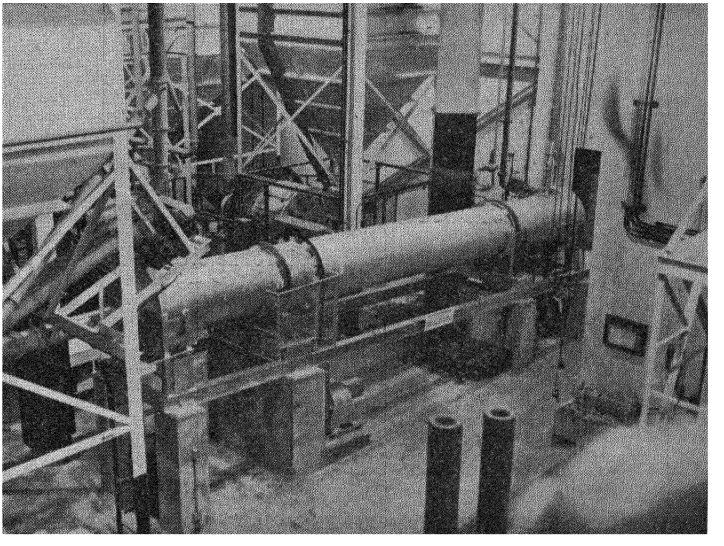

Fig. 3—Ore Heat Treating Kiln. Fine Grinding Mill in background.

fraction of the ground ore. Fully integrated automation has been applied to all ore handling operations.

Concentrated sulfuric acid (93% H_2SO_4) is used for sulfating the ground beryl ore, and consequently plain steel equipment can be used with no difficulty from corrosion.

The ground ore is weighed into batches and then mixed to a smooth slurry with concentrated sulfuric acid. The amount of acid used is chemically equivalent to the beryllium and aluminum contents of the beryl ore being sulfated. The ore-acid slurry is pumped in a small jet into the preheated sulfating reactor (Fig. 4), which is an autogenous lined, gasfired, plain steel mill. Prior to introducing the ore- acid slurry, the mill is heated to a temperature between 250° and 300°C (485° and 575°F).

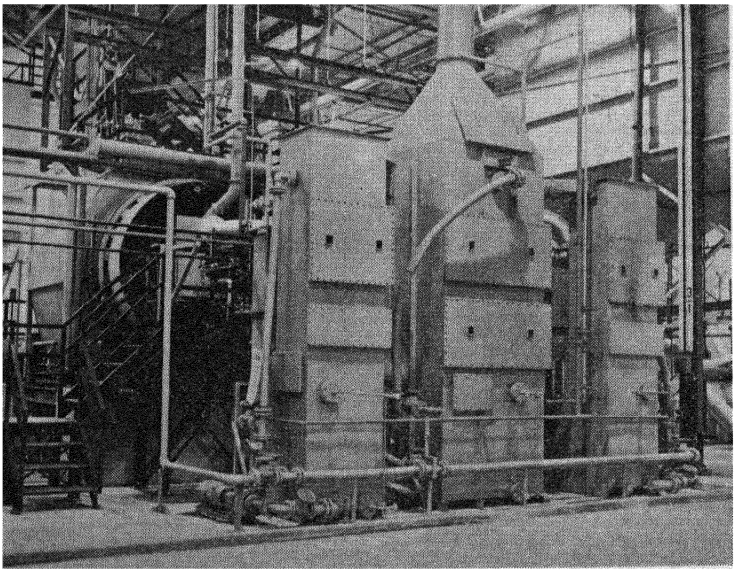

Fig. 4—Sulphating Mill at left. Sodium Carbonate Scrubbing Towers in foreground.

The technique of continuously impinging a small stream of ore-acid slurry on the preheated surface gives nearly instantaneous reaction, with consistent sulfate conversion yields in excess of 90 per cent.

The exhaust gases from the sulfating reaction are largely a mixture of SO_2, SO_3, and combustion gas, and they carry some ore fines. These gases are passed first through a Cyclone separator, where practically complete recovery of the fines is effected, and then into two packed scrubbing towers in a series where the SO_2 and SO_3 content is absorbed in sodium carbonate solution.

After sulfating, the ore is water leached in a five stage counter-current Dorr Thickener system which gives a leaching efficiency in excess of 99 per cent.

Pregnant liquor coming from the leaching system has the following nominal analysis :

Be	...	13	g/l
Al	...	15	g/l
Fe	...	2	g/l
Si	...	0. 1	g/l
H_2SO_4	...	1	Normal

Purification and Hydroxide Production

Theory and Background : A great many methods have been proposed for separating the beryllium content from solutions typified by the analysis above. All of the proposed purification processes can be divided into two basic types; those based on fractional crystallization and those based on fractional precipitation. Most commercial beryl-

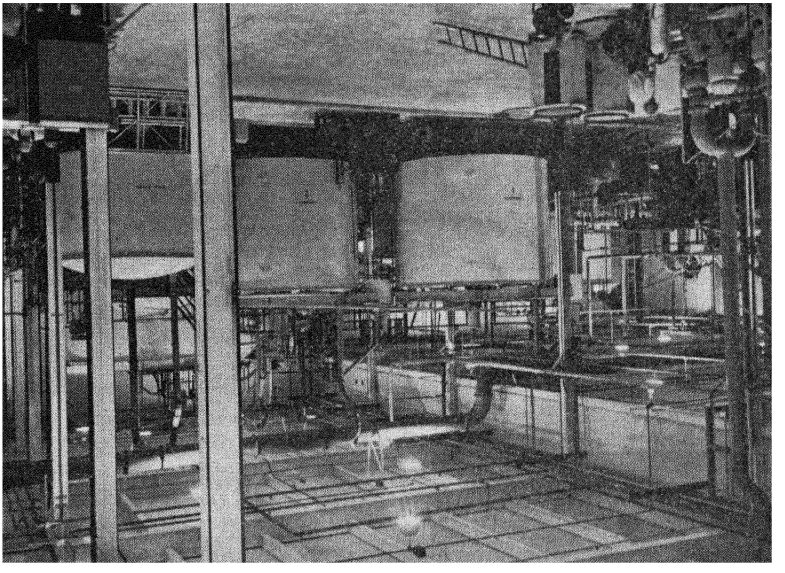

Fig. 5—General view of ore leaching and beryllium hydroxide production equipment—Dorr thickeners at center, hydroxide equipment, left edge.

lium sulfate processes have been hybrids of these two types, but nevertheless, the commercial processes can be readily placed by their basic principles into one or the other of these two categories.

The attractiveness of the fractional crystallization processes lies in their low reagent requirements.

The advantages of the precipitation processes are their simplified flow sheet and less complex plant machinery, and because most of the purification is done in only mildly corrosive basic solutions, a lesser maintenance cost. Until very recently, all of the fractional precipitation process required precipitation and separation of iron, aluminum and beryllium as hydroxides at some point in the flow sheet.

Developments in recent years in chelation chemistry have made possible major improvements in the precipitation processes. It is now much more economical in both operations costs and plant equipment costs to convert the impurities into water-soluble complexes so as to permit precipitation of the beryllium hydroxide while the impurities remain in solution.

Two types of beryllium hydroxide are generally recognized, and the product of the precipitation processes has always been either wholly the slimy β hydroxide or a mixture of β with some granular α hydroxide. The β form is precipitated by ammonium hydroxide or by sodium hydroxide at moderately basic pH, while the α form is precipitated from a strongly basic solution of sodium beryllate by boiling. Commercial practice has favored precipitation of the β form because alkali consumption is only half as great as is the case when α hydroxide is produced. However, the β hydroxide has poor filtration characteristics, and cannot be washed to high purity. Also, it does not readily lend itself to continuous production techniques.

Until very recently, The Brush Beryllium Company's processing has been based upon fractional crystallization. The recent advances in chelation chemistry mentioned above, and the ready availability of suitable organic sequestrants at reasonable cost, encouraged re-evaluation of precipitation processes. A research program was initiated as a result of this re-evaluation, and from this research has come a completely new type of precipitation process. The process developed by the Brush Beryllium Company permits precipitation of high-purity beryllium hydroxide without the necessity of physically removing any impurities from the solution. In addition the product of this process normally contains less than 15 percent water.

In the first step of the Brush process, the bulk of the aluminum is crystallized out as ammonium alum. The aluminum not removed by crystallization is eliminated as sodium aluminate in subsequent operations. Following alum crystallization, chelating compounds are added to the mother liquor as required by the end use of the hydroxide, so as to hold the undesirable impurities in solution. Excess sodium hydroxide is then added to convert the aluminum and beryllium to aluminate and beryllate respectively. Both of these compounds are quite soluble in cold alkaline solution, but they differ in that the beryllate decomposes

on boiling to precipitate α beryllium hydroxide, whereas the aluminate is unaffected. This difference makes possible precipitation of beryllium hydroxide without contamination by the aluminum remaining in the mother liquor from the primary alum crystallization step. Conversion of beryllium sulfate to beryllium hydroxide takes place according to the three reactions below :

$$BeSO_4 + 2NaOH \longrightarrow Na_2SO_4 + Be(OH)_2$$
$$Be(OH)_2\ (\beta) + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$
$$Na_2BeO_2 + H_2O \longrightarrow 2NaOH + Be(OH)_2\ (\alpha)$$

The normal beryllium yield in this process is 97 per cent.

All chemical processing is continuous and fully automated. The instrumentation required is shown in Figure 6. All plant operations are controlled from this control panel, including starting and stopping of all process equipment and all valve operation. The instrumentation includes "proper operation," indicators on all process steps and automatic "faulty operation" cut-off controllers.

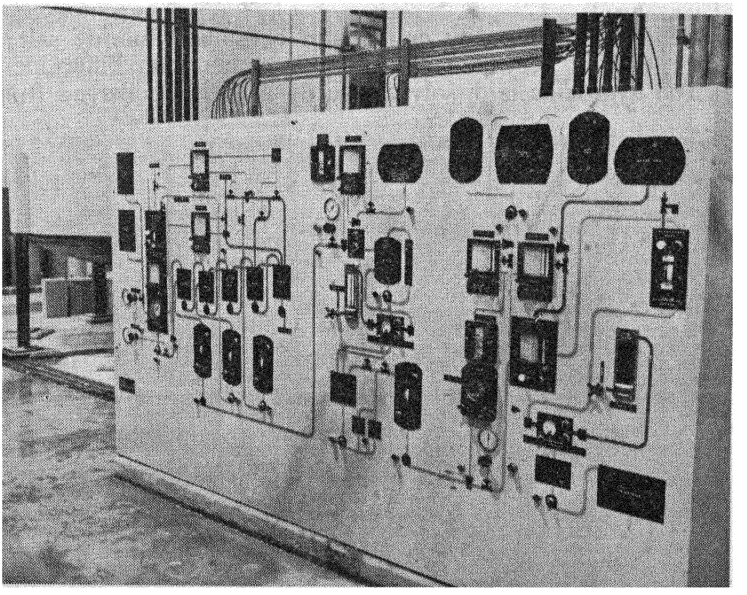

Fig. 6—Hydroxide Plant Control Panel. All chemical operations in manufacture of beryllium hydroxide are controlled from this panel.

Beryllium hydroxide produced by this process will normally come off the Bird centrifugal with a moisture content of 5 to 15 per cent, or a beryllium content of between 17 and 20 per cent. The impurity content is varied, depending upon requirements. Standard quality beryllium hydroxide contains, on a BeO basis, approximately .05% Fe, .15% Al, .05% Si, and .15% Na.

Production of Beryllium Fluoride and Thermochemical Reduction to Beryllium Metal

The Brush Beryllium Company's process, Figure 8 (Flow Sheet), which is the only one based on magnesium reduction of beryllium fluoride that has been operated for large scale commercial production of pure beryllium for any period of time, can be divided into four basic steps :

1. Production of high-purity ammonium beryllium fluoride salt,
2. Thermal decomposition of ammonium beryllium fluoride to beryllium fluoride,
3. Reduction of beryllium fluoride to beryllium metal with magnesium metal, and
4. Vacuum Casting.

Ammonium Beryllium Fluoride

Production of high-purity ammonium beryllium fluoride salt starts with dissolving of beryllium hydroxide in ammonium bifluoride solution. The hydroxide is dissolved directly as it is discharged from the

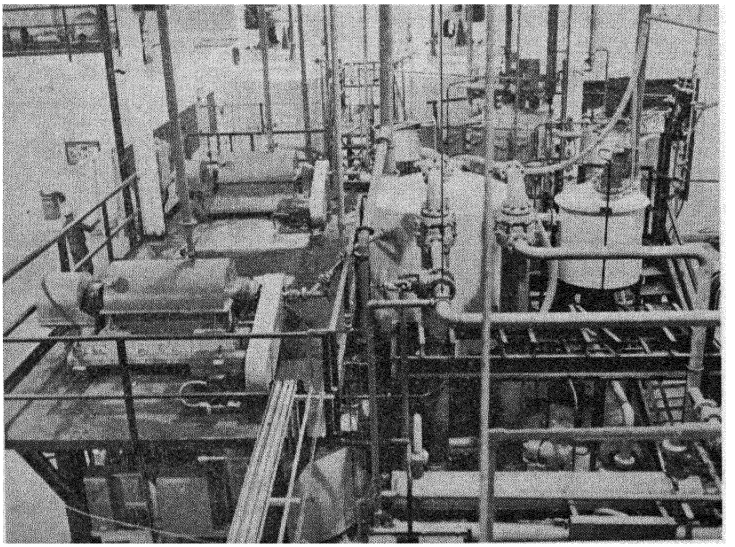

Fig. 7—Alum Crystallizer and Continuous Centrifuge in foreground. Beryllation kettle and hydrolizer behind crystallizer, with beryllium hydroxide centrifuge at left. Production capacity of of this equipment is approximately 1,000 lb. of beryllium per day. Large tanks in background are ammonium beryllium fluoride solution storage tanks.

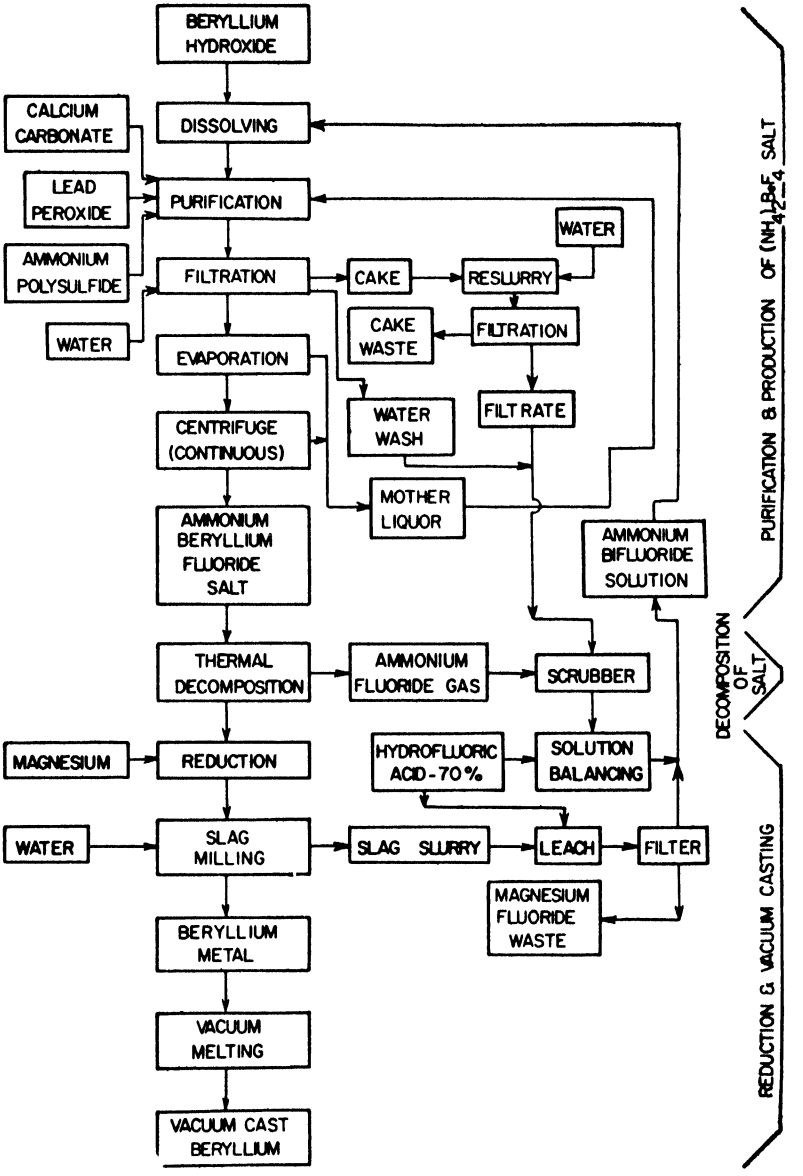

Fig. 8—Flow Sheet.

beryllium hydroxide centrifuge. This produces a solution of ammonium beryllium fluoride, $(NH_4)_2\ BeF_4$.

This compound has certain unusual chemical properties that make it ideally suited for purification by precipitation chemistry techniques.

Even at very low concentrations, ammonium beryllium fluoride does not dissociate to any appreciable extent. Consequently, there are so few

Be^{++} ions in solution that the solubility product of beryllium hydroxide cannot be exceeded. It is therefore possible to adjust the pH of the ammonium beryllium fluoride solution to any value desired for purification purposes without the danger of losing any beryllium as beryllium hydroxide precipitate. The latitude of treating procedures thereby made available makes it possible to produce ammonium beryllium fluoride of very high purity from virtually any type of feed material.

The solution is stored in rubber-lined steel tanks, where a check is made on the ammonium fluoride: beryllium fluoride ratio. Ammonium fluoride solution is added as required to bring the ammonium fluoride content to approximately 90 per cent of the stoichiometric requirement. Balanced solution is transferred to Haveg tanks provided with external heat exchangers. Here the solution is heated to boiling and calcium carbonate flour is added on an empirical basis to remove aluminum contamination.

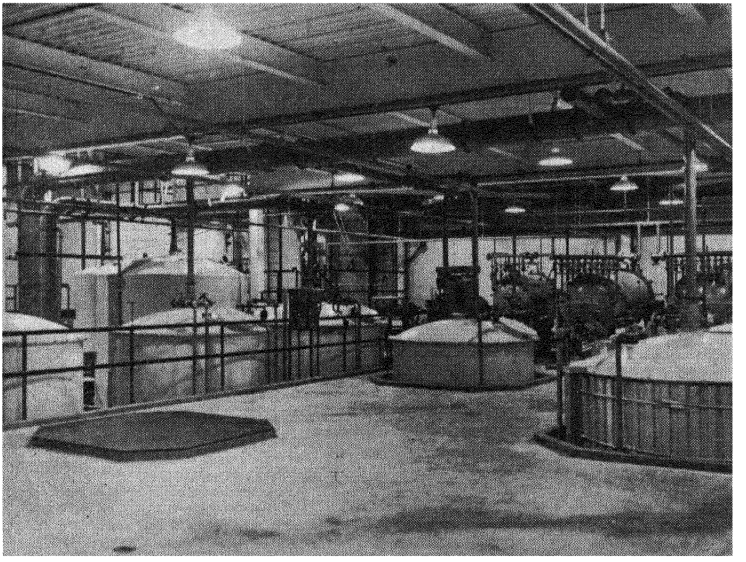

Fig. 9—Ammonium Beryllium Fluoride Solution Purification Area. Self-cleaning filters used for impurity separation in right background.

After the calcium carbonate addition has been completed, heating is discontinued and lead dioxide is added for removal of manganese and chromium. The resultant slurry is filtered through Sparkler self-cleaning, vertical-leaf pressure filters, provided with stainless steel filter screen. Prior to filtration, the filter screens are precoated with rayon

fibre. All filter parts that come in contact with the solution are made of Type 316 stainless steel, which has been found to be very resistant to corrosion by the ammonium beryllium fluoride solution. The pH of the solution at this point is approximately 8.3.

The main impurities left in the ammonium beryllium fluoride solution after treatment with lead dioxide and calcium carbonate are lead, nickel and copper. These are removed by treating the filtrate with ammonium polysulfide, whereupon these impurities precipitate as sulfides. The precipitated sulfides are filtered off in stainless steel Sparkler filters, and the filtrate is run into rubber-lined steel tanks, where the ammonium fluoride: beryllium fluoride ratio is again checked, and corrections made as indicated by the chemical analysis. The subsequent crystalization of ammonium beryllium fluoride salt proceeds best if the ammoniumfluoride: beryllium fluoride ratio is held as near as possible to stoichiometric requirements.

In order to insure the greatest possible purity of product, the filtrate from the sulfide filtration is given a polishing filtration through another

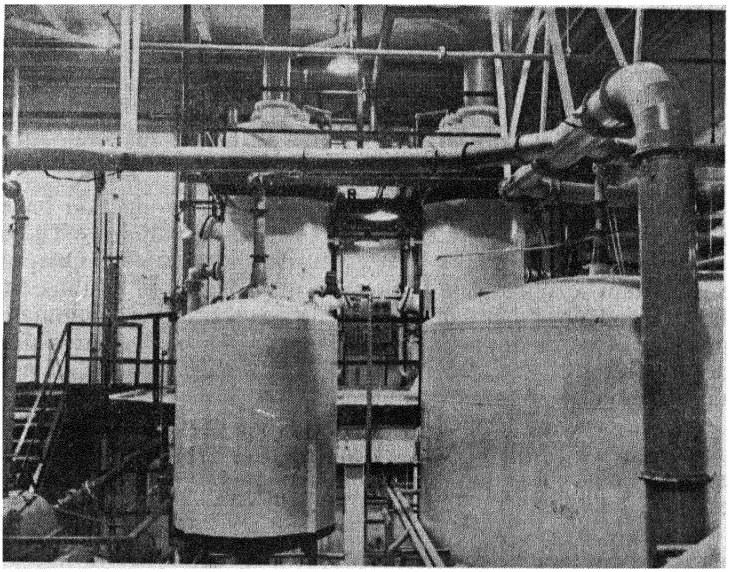

Fig. 10—Continuous Salting Evaporators. Automatic controls visible between evaporators. Continuous centrifuge at lower left corner. Evaporators operate at 2″ Hg absolute pressure, with 6,000 lb. per hour evaporation rate each.

stainless steel Sparkler filter as it is being transferred into the vacuum evaporator feed tank, which is of rubber-lined steel construction. Evaporation and crystallization are carried out simultaneously in a continuous salting vacuum evaporator of rubber-lined steel construction. The

heat for evaporation is supplied through an external tube-and-shell exchanger, which is provided with Karbate tubes.

In order to maintain smooth operation of the evaporation equipment, it is necessary that the per cent solids throughout the system be maintained at a low level. This is accomplished by continuously pumping from the evaporator body to a continuous solid bowl Bird centrifugal, where the salt is removed from the slurry and the filtrate is returned to the evaporator for further concentration. Because of the high purity of the evaporator feed liquor, it is not necessary here, as is ordinarily the case, to remove liquor from the system in order to maintain purity in the crystal product. All phases of evaporator operation are fully automatic. Washing of the salt is not necessary because of the high-purity feed liquor. Vacuum for the evaporator, which operates at approximately two inches mercury absolute pressure, is provided by a two-stage steam jet air ejector.

Beryllium Fluoride

Ammonium beryllium fluoride salt is readily decomposed thermally to ammonium fluoride and beryllium fluoride. This decomposition takes place slowly even at temperatures as low as 125°C (255°F). In practice, the decomposition is carried out at temperatures in the range 900° to 1100°C (1650° to 2010°F), yielding glassy beryllium fluoride and ammonium fluoride gas.

The health problems associated with beryllium production have forced a careful study of many of the production operations. These studies have resulted in many processing improvements. One of the more important technological improvements arising out of these studies has been the development of equipment for continuous automatic decomposition of ammonium beryllium fluoride salt to beryllium fluoride. In former practice, this decomposition was carried out in batches by addition of small amounts of ammonium beryllium fluoride periodically to a graphite crucible held at about 1000°C (1830°F). The crucible became progressively filled with liquid beryllium fluoride and finally had to be poured out, whereupon tremendous quantities of beryllium fluoride fumes were released.

Salt is fed continuously into the top of the continuous furnaces (Fig. 11), and as decomposition proceeds, liquid beryllium fluoride goes to the bottom of the crucible from which it is continuously drained through an overflow weir on to a casting wheel located below the furnace. Ammonium fluoride gas is taken off the top of the crucible into a packed scrubbing tower, and any ammonium fluoride not collected in the tower is caught in the Cottrell electrostatic precipitator above each scrubbing tower. Sump is used for scrub liquor. This equipment gives virtually 100 per cent yields of both beryllium fluoride and ammonium fluoride. The ammonium fluoride collected is treated in batches in Haveg tanks

with hydrofluoric acid to provide a solution of ammonium bifluoride, which is recycled to the dissolving operation.

Metal Reduction

Reduction of beryllium fluoride by magnesium takes place readily according to the equation :

$$BeF_2 + Mg \longrightarrow Be + MgF_2$$

The reaction proceeds rapidly at temperatures as low as 900°C (1650°F), but in order to separate the reaction products, the tempera-

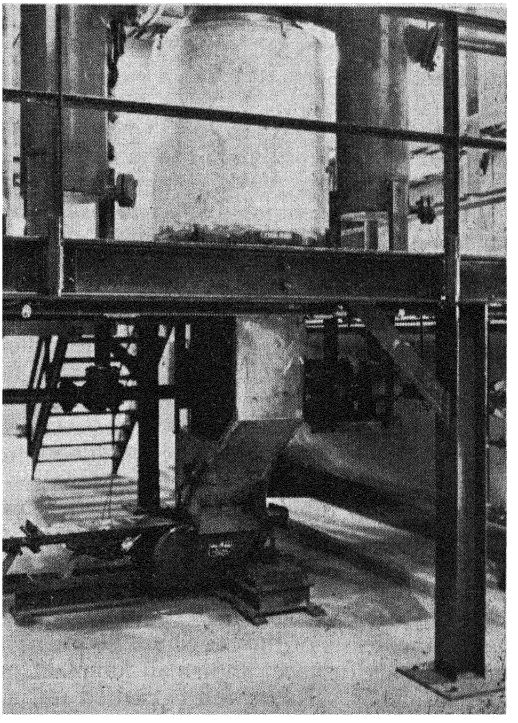

Fig. 11—Continuous Beryllium Fluoride Furnace on Platform. Casting wheel and BeF_2 conveyor below platform. Furnaces are 125 KW, 800 volt, 3,000 cycle units, with 50 lb. per hour BeF_2 production capacity.

ture must be raised to approximately 1300°C (2370°F), or above the melting point of magnesium fluoride and metallic beryllium. The reaction between magnesium and beryllium fluoride is strongly exothermic, but this can be controlled by care in operation.

If carried out in stoichiometric proportions, effective separation of the products is quite difficult. In commercial practice, this problem

is solved through the use of a substantial excess of beryllium fluoride in the reaction mixture. The maximum amount of magnesium that can be used consistent with good operation is approximately 75 per cent of the amount required stoichiometrically. With such a mix, the metallic beryllium separates readily from the slag, and a large part of the heat of reaction is dissipated in melting the feed materials. So long as there is sufficient excess of beryllium fluoride in the slag, the slag disintegrates rapidly on water leaching to release virtually all of the unreacted berylium fluoride into the leach water, which can then be recycled. In such a slag, the magnesium fluoride is found to be in the form of rather acicular crystals, each of which is encased in a film of beryllium fluoride which acts as a binder to cement the whole together. Under the action of hot water, the beryllium fluoride binder dissolves rapidly, causing the slag body to fall apart, thereby releasing the metallic beryllium particles.

When magnesium additions in excess of 75 per cent of stoichiometric requirements are used, the encapsulation of the magnesium fluoride crystals is incomplete, and therefore, the disintegration of the slag becomes more difficult. It is virtually impossible to separate metal from slag to any degree at all with mixes containing more than 85 per cent of the stoichiometric amount of magnesium.

Reduction of beryllium fluoride with magnesium metal is carried out in high-frequency furnaces provided with graphite crucibles. A graphite receiving pot is attached directly to the reduction furnace, so that at the end of the reaction the mix can be transferred into this receiving pot without contaminating the hood area excessively with beryllium fluoride fumes. In order to minimize air contamination, the reduction furnace is provided with a close-fitting primary ventilation system, which very effectively removes any fume released during the heating and reaction part of the operation cycle. In addition, the entire assembly is enclosed in a ventilated room, which need not be entered by the operators except momentarily.

The furnace charge consists of the beryllium fluoride pellets produced by the continuous fluoride furnace, and small lumps of magnesium, approximately one-inch cubes. Reduction is carried out as a batch operation, with a cycle time of approximately three and one-half hours at 75 to 100 KW power input to the furnace. The total charge consists of 260 pounds of beryllium fluoride and 96 pounds of magnesium.

Figure 12 is a photograph of the furnace used for carrying out the reduction operation. This furnace is a 100KW, 3,000 cycle induction furnace.

The filled crucible is covered and set aside to cool, after which the entire block of metal and slag is dumped into a large hammer-mill, from which the crushed material falls into a stainless steel ball mill for wet milling to separate the beryllium metal pebbles from the slag. Four

to five reduction batches are normally milled together. Approximately 31 pounds of metallic beryllium can be recovered from each furnace charge, which corresponds to a good materials yield of 62 per cent for the reduction furnace operation. The remainder of the beryllium is recycled to the purification operation.

In the milling operation, solution is pumped continuously through the mill at a controlled rate so as to carry out the fine magnesium fluoride crystals as they are liberated by milling. The solution leaving the mill goes to a tank where the magnesium fluoride crystals settle out, while

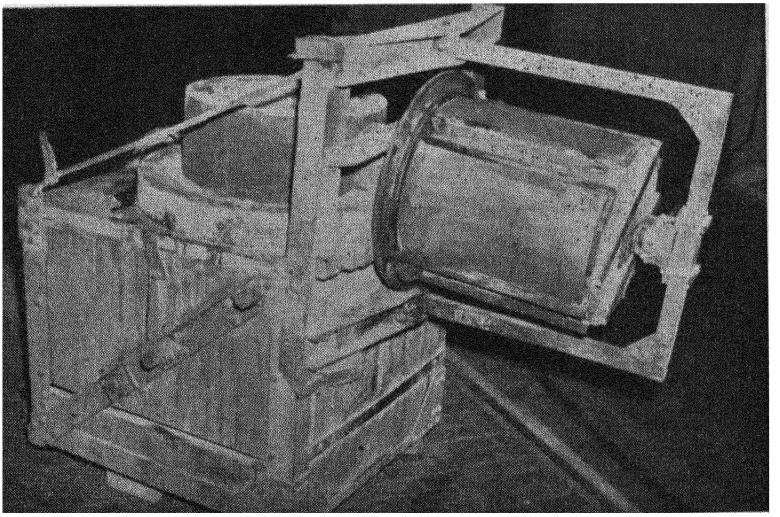

Fig. 12—100 KW, 800 volt, 3,000 cycle Reduction Furnace. Slag and metal receiving pot are tightly attached to furnace to eliminate fume generation during pouring.

the supernatant liquor is taken off the top of the tank and returned to the mill. When the beryllium content of the mill water has reached a sufficiently high level, the mill water circuit is switched to a second tank filled with fresh water.

In the course of milling, some metallic beryllium is worn off the surface of the beryllium pebbles and passes out of the mill along with the magnesium fluoride crystals. In order to recover the fine metallic beryllium, hydrofluoric acid is added to the tank contents, which are then reslurried in the tank with a turbine agitator. When all reaction has ceased, the magnesium fluoride is filtered off, washed, and discarded, and the combined filtrate and washings are recycled to the purification step.

The overall beryllium recovery in the reduction and milling operations is between 96 and 97 per cent.

In the milling operation small steel stars are used to increase the milling rate, and these become mixed with beryllium pebbles taken from the mill. These must be separated from the metallic beryllium. After drying, the mill charge is passed over a magnetic separator, which removes the steel milling stars.

Beryllium metal pebbles coming from this process will have an average metal content of approximately 97 per cent, with a total metallic impurities content, exclusive of magnesium, of from 0.2 to 0.5 per cent. The carbon content is approximately 200 parts per million, or about 600 ppm expressed as beryllium carbide, while the BeO content is about 0.1 per cent. The magnesium content, which will be present as both metallic magnesium and magnesium fluoride slag, may run as high as 1.5 per cent.

Vacuum Casting

Since beryllium metal produced by the magnesium-beryllium fluoride reaction may contain as much as 1.5 per cent magnesium, further processing is required before beryllium can be fed into the fabrication operations. Even small amounts of magnesium, on the order of 0.1 per cent, may affect the physical properties of fabricated beryllium adversely. Attempts have been made to reduce this magnesium contamination by melting the beryllium under slags containing large amounts of beryllium fluoride. While this technique effects a very substantial reduction in the magnesium content, it is still not good enough to satisfy the stringent fabrication requirements with respect to magnesium content. Therefore, vacuum melting is used to produce beryllium containing magnesium on the order of .03 to .05 per cent. Melting at absolute pressures of 300 to 500 microns will give beryllium castings containing less than 500 ppm magnesium. This residual magnesium content is not substantially reduced when melting is carried out at absolute pressures as low as 30 to 50 microns.

The furnace used by the Brush Beryllium Company for purification and production of powder metallurgy feed is shown in Figure 13. In this particular design, both the mold and the melting crucibles are contained within the evacuated space. The furnace is evacuated through one of the trunions. The crucible is so constructed as to automatically hold back slag and dross floating on the surface of the metal. In order to prevent contamination of the inside of the mold with vapors which condense in the furnace during the de-gassing part of the melting cycle, the mold is provided with a cover which can be removed from outside the furnace shell.

The vacuum furnace is a 3,000-cycle, 100-KW induction unit. Because of the vacuum employed, only 400 volts can be applied if corona is to be avoided. No graphite heating sleeve is employed and, therefore, heating is by direct induction into the charge.

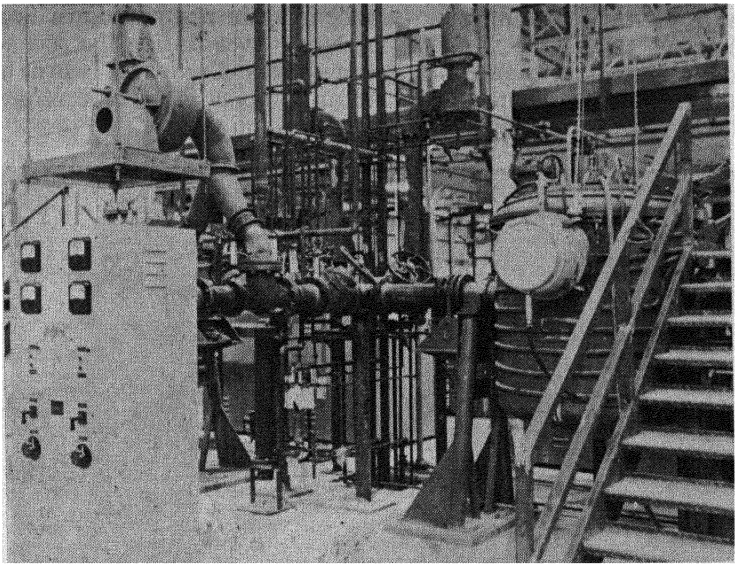

Fig. 13—Vacuum Casting Equipment. Light coloured attachment is mold container. Note ventilation system connection to furnace through trunion. This provides ventilation on furnace shell to make charging operation safe.

Graphite is used for mold material, and the size of ingot normally cast is 9 inches in diameter by 18 inches long, with a weight of 70 to 75 pounds. The operating cycle is five hours. A beryllium oxide crucible is used for melting, with beryllium oxide powder as insulation between the crucible and the high-frequency coils. This type of construction makes possible patching of cracked and eroded crucibles, and normal crucible life, therefore, ranges from 100 to 140 heats.

Because heating of the charge is by direct induction, small particles, such as machining chips, cannot be melted alone. When material of this type is to be vacuum melted, the crucible charge is made up of a mixture of the fine scrap and beryllium metal pebbles or large section scrap pieces.

The removable cover of the vacuum furnace is provided with a small diameter sight tube to permit observation of the melting operation, and this tube is so constructed as to permit easy removal of the sight glasses. This design feature is utilized to probe and skim the charge and also makes it possible to charge additional metal after the initial charge has melted down. In the operating cycle, after the initial charge has been put into the crucible and the mold cover put in place, the furnace is sealed, pumped down to vacuum, and power applied. When melting has proceeded nearly to completion, helium is admitted to the furnace, the sight glass is removed, and additional metal is added. The sight

glass is then replaced and the furnace is again pumped down to approximately 500 microns absolute pressure. It is during the second evacuation that most of the out-gassing takes place and, when melting metal of high slag content, the rate of pumping must be carefully controlled to avoid excessively violent gas evolution.

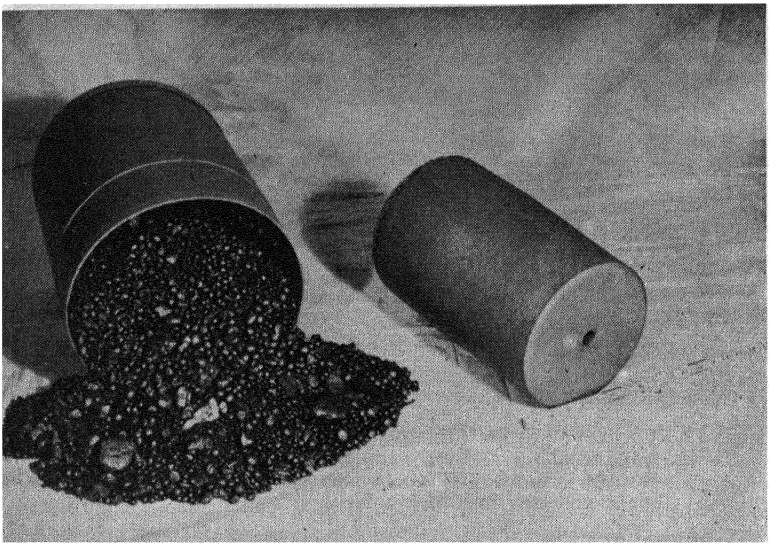

Fig. 14—Pure Beryllium Pebbles, left, and Nuclear Grade Vacuum Cast Ingot.

The progress of de-gassing can be readily observed through the sight glass and, when it has progressed to completion, the mold cover is removed by means of the reach rod and the molten charge is quickly poured into the graphite mold.

The vacuum system used consists of a five stage steam ejector with inter-condensers between the third and fourth stages.

The vacuum casting operation makes no change in the impurities in the beryllium metal charge, except for reducing the slag and magnesium contents.

There is some loss of the charge to the small amount of slag produced in this operation. As a result of this beryllium loss to the slag, the good materials yield from charged beryllium to finished vacuum casting is 90 per cent. The vacuum casting slag produced is recycled to the ammonium beryllium fluoride dissolving step, and this gives an overall beryllium recovery in the vacuum casting operation of 95 per cent.

On the average, the assay of vacuum cast ingots will be 99.5 per cent as a minimum, while the magnesium content will average between 0.03

and 0.05 per cent. Table I gives the complete analysis of a vacuum casting typical of metal produced by the Brush process.

Table I: Analysis of typical vacuum cast Ingot

Be, %	99.5
C, ppm	400
Fe, ppm	1100
Mn, ppm	70
Cr, ppm	90
Ni, ppm	130
Mg, ppm	500
Al, ppm	600
B, ppm	1.2
Cd, ppm	<0.5
Li, ppm	<1
Ag, ppm	<5
Co, ppm	Approx. 2

Discussions

Dr. B. C. Kar, (*N. M. L., Jamshedpur*) : Would anybody care to comment whether there is any relation between purity and ductility of the beryllium metal? Is brittleness due to impurities present?

Mr. L. M. Wyatt, (*U.K.*) : Regarding Dr. Kar's question on the brittleness of beryllium, this can best be answered by reference to the properties of a single crystal.

This has very anisotropic characteristics and can deform by twinning in one direction, but a stress in another direction will produce cleavage.

Therefore in a coarse grained specimen applied stress is certain to cause fracture in at least one grain which will propagate throughout the specimen.

High ductilities are possible in one direction in worked rods, or in two directions in cross rolled sheet.

In addition it should be possible to produce material with ductility in all directions if the grains are random and sufficiently fine, and some strain can be accommodated at the grain boundaries.

Dr. R. Caillat, (*France*) : I may add that Pechiney in France have used this principle in the production of ductile extruded tube by a process of casting, comminution, compaction and extrusion.

PRESENT STATUS OF PRODUCTION OF METALLIC URANIUM AND THORIUM

*By S. K. Kantan and G. S. Tendolkar**

ABSTRACT

A brief outline of the processes used for the production of uranium and thorium is given. The different trends towards improving the efficiency of the processes and the purity of the product are also indicated.

Uranium is the only naturally occurring nuclear fuel. It contains about 0.7 percent U^{235} which is fissionable. Any atomic energy programme depends primarily on uranium as a fuel. On the other hand, thorium is a fertile material and finds use in breeder or convertor reactors in which thorium is converted into U^{233} which is fissionable.

Both uranium and thorium are produced from reduction of their compounds by either chemical or electrolytic methods.[1-8, 31-35] Practically every possible method of reduction has been tried and the most suitable ones have been adopted on a commercial scale.

The production of both the metals is associated with many difficulties attributed to the stability of their compounds[11-13] and the consequent reactivity of the metals towards most materials of construction especially at high temperatures. In general the reductions appearing to have better chances of success are the reductions of oxides or halides by either chemical or electrochemical means (fused bath). The electrodeposition of both the metals from aqueous or organic solutions of their compounds though claimed in a number of patents has not been attempted on a commercial scale [1,51-57].

The chances of getting the metals in a massive consolidated form are greater in the case of halide reduction by chemical means. The oxide reduction and electrolytic reduction (of halides) yield the metal in the form of a powder. With the growing importance of powder metallurgy techniques in the fabrication of fuel elements,[52,53] the production of metals in the form of powder may not be a serious drawback. Further, whereas chemical methods of reduction are not self-refining it is found that some of the impurities can be removed in the course of electrolytic reduction.

The important considerations behind the reduction processes of uranium and thorium are discussed at a great length in various Geneva papers [12, 25, 27, 28, 33, 41] and in the books[3-4] subsequently published. The present paper gives a brief outline of the processes used for the

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production of uranium and thorium and reviews the recent developments.

Uranium

Current Production Methods : Though the first few tons of uranium used for the Manhattan Project[51] were reportedly made by electrolysis of fused halides, at present almost all the uranium is made by the reduction of uranium tetrafluoride by either magnesium or calcium[25-30], and there is a tendency amongst those countries using calcium reduction to change over to the magnesium reduction process. The cost of magnesium is only about 1/5-1/10 of the cost of calcium and a smaller proportional weight of magnesium is required. This would reduce the cost appreciably. However, because of the high vapour pressure of magnesium at the temperature attained in the reaction, the reduction is carried out in a closed bomb. The process has also a lower heat of reaction and hence it is necessary to add extra heat to the reaction either by the use of boosters or by preheating the charge to about 600°C as is usually done. It may also be noted that whereas good yield of metal can be obtained by calcium reduction with a UF_4 of only 96% purity, for magnesium reduction the UF_4 should analyse at least 98%.

Magnesium reduction process has been used in U.S.A.[10, 28] and more recently has been adopted in U.K.[30, 15]. It appears that calcium reduction is still practised in France, Belgium and U.S.S.R.

A typical flow sheet for the production of uranium from crude uranyl nitrate given in fig. 1 incorporates the more important methods.

Improvements in the Process : The continuing demand for large quantities of pure uranium metal has promoted interest in the development of new and better processing techniques. The early stages of uranium production involved the use of large quantities of hydrogen peroxide. The improved methods of multistage counter current solvent extraction as also the precipitation of ammonium diuranate instead of uranium peroxide make it possible to eliminate the use of expensive reagent like hydrogen peroxide.

In the initial stages, the uranium tetrafluoride was made by wet process (i.e. reacting UO_2 with aqueous HF). This had to be dehydrated to dry UF_4 which had a low bulk density (1.8 g/c.c.). A dry process UF_4 gives a product with a higher bulk density (3.5 g/c.c.) and hence a higher capacity of the reduction units.

A technique for the continuous production of UO_3 from uranyl nitrate solution by fluidized calcination has recently been developed[49, 50]. This would obviate the ammonium diuranate precipitation stage. (*vide* fig. 1.) A fluidized bed technique has also been developed to produce uranium tetrafluoride[49]. A major advantage is that there is little limitation on the size of the fluidized bed reactor, and a uniform temperature

control can be achieved and heat removal simplified. The use of multi-stage reactor has been found to be considerably more efficient than single stage, particularly in the hydrofluorination step.

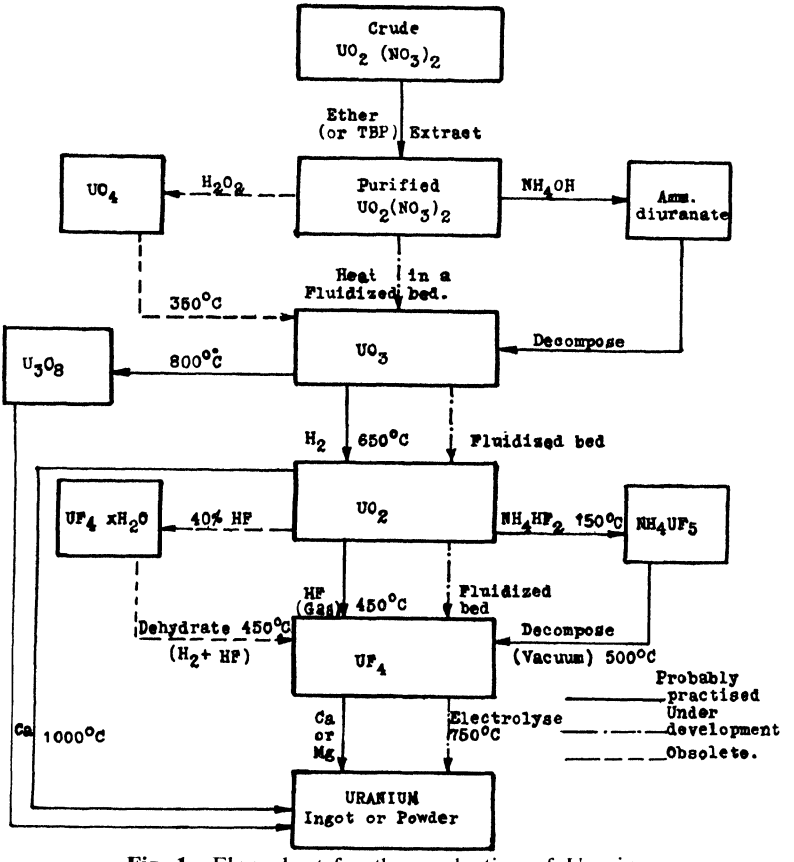

Fig. 1—Flow sheet for the production of Uranium

Attempts have been made to cast the uranium metal directly[28] from the reduction bomb with a view to eliminate the subsequent melting and casting operation. But it is doubtful whether the ingots so produced (because of high Mg & H_2 content) can be used directly in a reactor operating at a fairly high flux.

It is understood that a simple technique for production of uranium is practised in the U.S.S.R., namely, reduction of the fluoride with calcium in an open crucible without the use of any elaborate set up as is used in other countries. The size of the batch handled has to be, however, large-at least over a ton. It is also further understood that no subsequent vacuum melting is necessary in such a practice. If this has been possible then it shows a considerable advance on the existing

methods practised in other countries and may well make the technique of uranium production much simpler.

The reduction of uranium oxide although quite practicable[7, 14-16] has not been exploited on a commercial scale. Interest has been revived in the reduction of uranium oxide with calcium especially for the preparation of U^{233}. Glove box techniques have been developed and the reduction yields high purity uranium powder[17].

The use of zinc[16] in the preparation of uranium has been reported. It has been possible to reduce various uranium compounds with magnesium in a zinc solvent. The uranium is subsequently recovered from solution by the decomposition of the alloy UZn_9 formed in the reaction. Although the electrolytic method of preparation[18-20] has been superseded, it is gaining ground especially for the refining of uranium and for the preparation of high purity uranium.

In one of the methods[22] electrolytic reduction is carried out at 630°C, to yield high purity uranium from a bath consisting of 25-30% UCl_3 in a solvent containing 48% $BaCl_2$, 31% KCl and 21% NaCl. In another method[23] Uranium trichloride (UCl_3) is electrolysed in a fused mixture of LiCl—KCl at 400-425°C under an atmosphere of argon. The uranium produced is in the form of dentrites and after removal of the bath salts it is melted under vacuum to give metal containing only about 70 ppm total impurities.

The electrolytic reduction has also been adopted for the preparation of uranium from its oxide[21]. Moreover the process holds promise of being a continuous one. Normally the fused salt electrolysis of halides for the production of uranium (as well as thorium) is done at temperatures below the melting point of metal so that the final product is in the form of either a fine powder or dentrites. On the other hand the production of uranium by the electrolytic reduction of uranium oxides in fused salt is carried out at temperatures (1200-1250°C) above the melting point of uranium.

Refining of Uranium : Electrolytic methods have been developed for the refining of uranium [15,24]. It is claimed that uranium metal containing significant amounts of Fe, Cu, Cr, Mn, Ni, and Si may be electrolytically refined to near spectroscopic purity[24] in fused salt electrolyte containing 33 wt% UCl_3, 30% LiCl and 37% KCl. The electrolysis is done at 400-425°C under a protective atmosphere of argon or helium. Uranium anodes are employed and the product in crystal form is deposited on molybdenum or tantalum cathode. Uranium cathode may also be employed.

Several of contaminants of uranium can be removed or controlled by vacuum melting and liquation[24a] This is invariably done as the first step before the fabrication of uranium. The effect of various containers and also the distribution of impurities in the cast ingot are dis-

cussed in detail. Oxygen and nitrogen are rapidly removed by liquation and contents of less than 10 ppm are readily obtained. Iron and silicon are not removed. Under optimum conditions a metal is produced that will contain no more than 130-200 ppm total impurities.

Thorium

It is seen that the only method practised for the production of uranium on a commercial scale is the reduction of uranium tetrafluoride with either calcium or magnesium. On the other hand, in the case of thorium it is apparent that more than one method is in practice. The fluoride method of reduction (ThF_4+Ca) is not sufficiently exothermic and hence conditions have been modified to suitably facilitate the reduction step. However, the ultimate product is at best a sponge, which has again to be remelted. This does not offer a definite advantage over the reduction of the oxide with calcium or the electrolytic method of reduction of the halides, both of which yield the metal in the form of powder.

The methods of reduction of thorium compounds to thorium metal are indicated in fig. 2.

Reduction of Thoria with Calcium : Calcium reduction of thoria holds promise of being adopted on a large scale and it appears that it is practised in U.K.[65]. The reduction of thoria with calcium has been attempted by many workers with different modifications.[35-39] The control of particle size is an important factor. The reduction of thoria is done at a temperature of about 1100°C, much below the melting point of thorium (1695°C) and attempts have been made to use fluxes ($CaCl_2$) to regulate the particle size. By fluxing action the calcium chloride serves to increase the particle size of the thorium metal power and to render it crystalline rather than amorphous. This greatly reduces its pyrophoricity. Particle size is also increased by increasing reaction temperature and soaking time.

Reduction of Halides

Chemical : The reduction of thorium tetrafluoride with calcium is practised in U.S.A. on a commercial scale[33,35a] The reaction is not sufficiently exothermic to keep the products of reaction molten. Hence zinc chloride is added to the reaction mass. In addition zinc forms an alloy with thorium (5-6% Zn) to give a lower melting phase and the calcium chloride fluxes the calcium fluoride slag. The zinc is distilled off under vacuum from the thorium zinc alloy at 1100°C under a pressure of less than 200 microns, leaving the metal thorium as a sponge.

It was known that the $ThF_4 \times H_2O$ precipitated from aqueous solutions was difficult to dehydrate[47]. It was hence thought necessary to prepare the ThF_4 by the dry way process. It was subsequently shown[48] that $ThF_4 \times H_2O$ could be successfully dehydrated at about 400°C in

an inert atmosphere. ThF_4 in order to be safe for bomb reduction should contain $<0.1\%$ moisture.

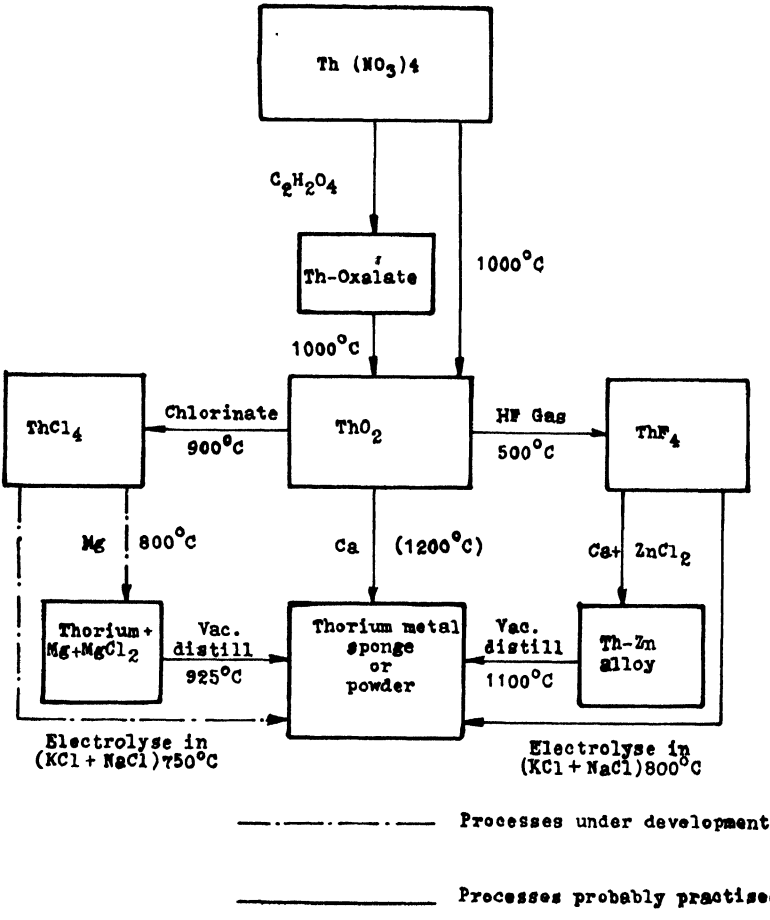

Fig. 2—Flow sheet for the production of Thorium

In the foregoing method of reduction, the zinc chloride used is hygroscopic and hence is a potential source of oxygen. Preliminary work on an experimental scale using zinc and iodine instead of zinc chloride has shown satisfactory results[44].

The reduction of a charge consisting of 30 parts of granular calcium, 70 parts $ThCl_4$ and 30 parts $ThOCl_2$ has been reported[39a]. The conditions for reaction and subsequent processing are closely related to the reduction of thoria with calcium and the process yields a high purity product.

The reduction of thorium tetrachloride or thorium tetrafluoride with

calcium and with the addition of sulphur as a booster with varying degree of success has been reported[34]. The worst feature of the process, however, was the low purity of the metal produced.

Electrolytic : The electrolytic method of preparation of thorium from fused salt bath appears to be practised as a regular production method by U.S.S.R.[41]. The electrolysis reduces the rare earth impurities and results in considerable purification of the metal. With a current density of about 20 amp/dm^2 a stable yield is obtained at a current efficiency of 70-80%. The bath consists of thorium tetrafluoride dissolved in a mixture of fused sodium and potassium chlorides. The effect of temperature was studied and the optimum particle size for powder metallurgy at 70-80% current efficiency was obtained at 800°C. Bath containing more than 11% of thorium is preferable.

The electrolytic method of reduction has been attempted by some other workers.[40,42,43]. In U.S. also the electrolysis of potassium thorium fluoride in sodium chloride has been done on a pilot plant scale[42].

Recent Developments

Attempts have been made to base a continuous process on the system $ThCl_4$ in NaCl or NaCl-KCl molten bath[35a]. An interesting feature of this method is that the thorium tetra-chloride is prepared in situ in the molten bath itself. Major improvements have been the development of a water cooled cathode with an air cooled tip to control deposit adherence, a system for withdrawal and unloading of a loaded cathode without breaking the atmosphere seal, and co-ordination of cell feed preparation with electrolytic cell additions and withdrawal to give a semi-continuous process.

More recently attempts have been made to adapt the Kroll reduction technique for the production of thorium[35a]. In the Ames method $ThCl_4$ purified by double distillation was heated to 900°C with a 100% excess of magnesium under argon in a tantalum or titanium crucible to produce a thorium-magnesium alloy which segregated massively and separated well from slag. Excess magnesium and adhering $MgCl_2$ were removed by vacuum distillation at 925°C leaving the thorium as a sponge.

The U.S. Bureau of Mines,[35a] overcame one of the problems of contamination inherent in the above method by volatilizing the salt phase thereby carrying out the reduction in vapour phase (of $ThCl_4$). The thorum tetrachloride was volatilized at temperatures from 825 to 925°C. The reaction was done under one atmosphere of argon with 65% excess of molten magnesium at temperatures of 750 to 820°C

producing a sponge. A major problem in the reaction step appeared to be the extreme corrosiveness of $ThCl_4$ at temperatures required for volatilization and the difficulty of obtaining $ThCl_4$ of sufficient purity to hold down the oxide content of the metal product.

The Oak Ridge National Laboratory[35a] has developed a process usually termed the Metallux amalgam reduction, in which anhydrous thorium tetrachloride is reduced to metal by sodium amalgam. The purity of the thorium tetrachloride with respect to oxide, oxychloride and carbon is not very critical. The amalgam thorium mercuride is heated in vacuum retorts at a pressure of 1 micron. The thorium is left in the form of a massive ingot. Ductile metal R B hardness O to 20, having a density of 11.67, ThO_2 by HCl insoluble 0.6-1% and a carbon content of 100-400 ppm were reported.

Purity of Metals

The foregoing review indicates the various problems in the production of uranium and thorium and the attempts made to solve some of them. Among the considerations in the production are not only the cost of production but also the high purity of the final metal.

The purity of the materials required for atomic energy purposes is very rigid and even surpasses in some respects the exacting standards set for pharmaceutical products. Though there is no rigid definition for nuclear purity a term 'Boron equivalent' is used to specify the amount of impurities objectionable nuclearwise. This gives a measure of the parasitic absorption of neutrons by the impurities. The value of boron equivalent should be very low, of the order of less than 1 ppm for nuclear fuels and the actual value to be attained in any fuel production has to be based on the relative cost of purification of the metal and the cost of the resultant critical mass.

Some impurities although not objectionable from a nuclear point of view, alter the physical and mechanical characteristics of the metal to a marked degree. The impurities have to be kept below certain limits to ensure desirable metallurgical properties such as grain size, ease of fabrication and the ability to withstand the severe conditions encountered in a reactor. Tables 1 & 2 give the typical analysis of some of the samples of uranium and thorium metals, produced in variout places.

Some Production Data

The production of uranium has made vast strides, although the industry is only about 15 years old. The cloak of security that has shrouded the production of uranium and thorium since the early days of world war II has recently been partially lifted and details of output

TABLE 1: Analysis of Uranium [23,25,26,30,59]

Prepared at	Composition in ppm.											
	C	N	O	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Si
Bouchet Plant[25]					20 —			50 —		5 —		100 —
Ca reduced					50			200		10		500
ANL. Mg. reduced	8 — 13	19	—	5	20	5	1	20	15	1	10	15
ANL. Mg. reduced re-melted in graphite.	240 — 295	10 — 16	6 — 16	10	20	2	5	30	0.5	2	15	15
Belgium Ca[26] reduced re-melted in Alumina	40	7	16	20	—	5	3	28	5	8	5	10
British[30] Ca reduced	800 200	100		300				175 100				
Mg. reduced	— 300											
High purity[23] uranium	16	10	8	5	—	1	2	2	0.5	0.5		3 — 5
									K 10	Li 1	Cl 6	

TABLE 2: Analysis of Thorium [2,38,58,59]

Prepared by	Composition in ppm.											
	C	O	N	Al	Si	Fe	Be	H	Ca	F	Na	Cl
Ames Iodide Th[58]	370	120	150	90	90	140	30	100				
	200	110	10	Tra-ce	Tra-ce	Tra-ce	100	100				
Iodide Th[58]	40	50	20									
Ca reduced	500 —	200 —	100 —	100		250 —		50 —				
Th. U.S.A.	1000	1300	200			350		150				
U.S.S.R.[38]			50 —			200 —			1000 —	200 —	20 —	20 —
			170			400			2000	500	50	30
Ca reduced[2]	150 —	200 —	150 —		300 —	300 —			300 —			
	200	600	200		500	500			500			
Electrolytic Th			30 —			240 —			30	2000 —	30 —	30 —
U.S.S.R.[38]			100			600				4000	100	150
Electrolytic[2]	100 —	200 —			300 —	100 —						Mo
	200	600			500	200						10/50
Crucible melted Th		70 —	20 —					1 —				
		80	30					1.5				

and reserves are now available for some principal producers, such as U.S.A., Canada, France & Australia (Table 3.).

TABLE 3: Production of Uranium [45,60,63]

Countries.	1956	1957	1958	Expected 1959	1975
World ..	15,000		30,000	40,000	100,000
U. S. A. ..	6,000		12,000	—	
Canada ..	3,000				
France ..		300			3,900
Australia ..		1,000 (Oxide)			

The recently released data indicate that the production of uranium was about 15,000 tons in 1956 (and about 4,000 tons in U.S.S.R. and other East European countries) and is expected to be doubled in 1958 when projected plants and plants under construction are completed. The current price of uranium is reported to be $. 18/lb. However, it may be noted that there is a Japanese claim[64] that uranium could be produced by electrolytic process at 2,000 yen per Kg. ($. 6|Kg).

Thorium is used presently in various forms (metal, oxide and oxycarbonate) in the reactors and the exact figures for the production of the metal are not available. It is reported[61] that in 1956, Consolidated Edison Co. had purchased from U.S. A.E.C. about 12 tons of thorium metal for $537,000. According to Howe[62] U.S. will need about 60 tons of thorium (metal and its compounds) by 1960 for its reactor programmes, and the demand is likely to go up to 11,000 tons by 1975.

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Discussions

Dr. R. Caillat, (*France*) : I should like to complete the interesting report of Messrs: Kantan and Tendolkar with a few indications on the reduction of UO_2 and ThO_2.

At Saclay, we proceed to the reduction of UO_2 both by Ca and by Mg. Although it is only a laboratory-scale production, the plant may give upto 1 ton of metal per month.

We are dealing with a furance under an argon atmosphere, con tinually supplied with compressed tablets of oxide and calcium. The arrangement adopted makes it possible to avoid any contamination ; the compressed tables rest on sintered lime plates. After reaction, the mixture of powdered uranium and lime is treated chemically. The uranium powder isolated in this manner is stabilised. In this way, the manipulation of pyrophoric uranium is avoided. The uranium powder contains less than 0.5% of uranium oxide.

It is used either for the preparation of objects in sintered uranium, or in the preparation of uranium carbide UC, and also for the preparation of U—UC cermets.

We have been able to obtain, in particular, sintering of uranium carbide UC of density very close to the theoretical density, without open porosity. The reduction may also be carried out with magnesium.

The same furnace may be used to manufacture powdered thorium, which is easily transformed into bars and plates.

Dr. B. C. Kar, (*N. M. L. Jamshedpur*) : Is it possible to reduce UO_2 and ThO_2 by carbon ?

Dr. Caillat, (*France*): We have had occasion to take up a study which Kroll had published before the last war on the reduction under vacuum of uranium oxide by carbon. In every case, the reaction led us, contrary to what might have been hoped from the investigation by Kroll, to a uranium strongly charged with carbide UC.

Dr. Brahm Prakash, (*Atomic Energy Establishment, Bombay*): Both thorium and uranium oxides have unfavourable free energies in their reaction with carbon although this is counterbalanced by the formation of a gaseous reaction production (CO) which can be continuously removed by vacuum, thereby upsetting the equilibrium. In the case of UO_2 reduction in graphite crucibles, the resulting product consists of uranium and uranium carbide since carbon is virtually insoluble in uranium to a composition of 50 atomic percent. There are indications that methods of separating the carbide phase from the uranium phase may be successful. In the case of thoria reduction, however, this segregation into two phases does not occur and the final product even after long annealing periods is still a mixture of thorium-carbon solid solution and thorium carbide, rather than pure metal and carbide.

PROBLEMS IN TREATMENT OF IRRADIATED FUEL ELEMENTS AND BREEDER BLANKETS

*By Rajindra Manocha**

ABSTRACT

The treatment of irradiated fuels and breeder blankets resorted to for the recovery of fissionable material from irradiated charges constitutes one of the most important links in any programme of large scale exploitation of atomic energy. Such treatment has problems peculiar to itself—many of them not encountered in any other type of plan—mainly on account of high levels of associated radioactivity. This paper seeks to draw attention to their nature and indicate in a general way how they influence the philosophy of treatment programmes, selection of separation processes, cycle of operation, design and equipment.

Fuels used in atomic energy reactors can be burnt only to a limited extent leaving even in most favourable conditions the major part of fission material unutlised and to be recycled. This limitation on burn-up is necessitated for various reasons : splitting of one atom of uranium gives rise within the atomic lattice to two (different) atoms possessing high kinetic energy. The fission products generally include about 10 per cent of permanent gases. The natural consequence is distortion in the atomic lattice and generation of destructive stresses in the fuel element assembly. Further, some fission products have high neutron absorption cross section: such products act as poisons and tend to bring the process of fission to stop by absorbing and removing the neutrons required for sustaining the chain reaction. One percent of burn-up, introduces about 2 percent of impurities in the fuel element[1]. Reprocessing of the fuel has then to be undertaken to salvage the fuel from these poisoning elements and/or other damaging constituents and no programme of nuclear energy exploitation can be envisaged without this step.

Besides, in every reactor, due to interaction of neutrons there is some formation of fissionable material taking place: uranium-238 gets converted to plutonium and thorium-232 to uranium-233. Since these breeder products are as good sources of atomic energy as uranium-235 itself, and it is generally conceded that the amount of uranium-235 which is readily available is not great enough to contribute substantially to the present energy requirement of the human race, their recovery becomes of paramount importance. Further, it has an important economic bearing on nuclear power generation: 1 gram of plutonium costs $30 to $45 and 1 gram of uranium-233 produced from thorium[2] about $ 15 and without debiting this to the credit side, generation of power would not be economically feasible.

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Reprocessing of the irradiated fuel and breeder blankets has problems peculiar to itself, unique in the sense that they are not encountered in any other type of plant and it is the purpose of this paper to draw attention to their nature and indicate how they influence the selection of separation processes, cycle of operation, design and equipment. The problems are mostly caused by associated radio-activity which could very easily be equivalent to tons of radium. Resultant unit cost for even a sizable plant processing comparatively simple forms of irradiated material is at least five times the cost which would obtain if non-actives were to be similarly processed[3]. These problems could apparently be resolved by allowing the radio-activity to decay with time. This is, however, a slow process and the time required for the purpose is to be considered in terms of mounting inventory charges resulting from high cost of uranium, plutonium, thorium etc.

The word "charge" wherever occurring in the text below is meant to cover both the fuel and breeder blankets.

Elements involved in the charge

The composition of the charge will vary with the type of reactor and duration of run. Fission products are a mixture of isotopes of more than 30 elements, mostly rare earths, their atomic numbers ranging from 30—64.

Table I given below will serve to convey an idea about the order of preponderance of various fission products with respect to each other[8]. This is based on a fuel from reactor using natural uranium and the charge has cooled for 100 days.

Table I

Strontium	*	3.8%	Zirconium	*	9.9%
Barium	*	4.0%	Niobium	*	4.7%
Yttrium	*	2.3%	Tellurium	*	1.2%
Lanthanium	*	4.0%	Iodine	*	0.6%
Cerium	*	10.1%	Ruthenium	*	5.0%
Neodymium		10.0%	Xenon		10.0%
Cesium		10.0%	Molybdenum		8.0%
Praseodymium		4.5%	Samarium		3.0%
Technetium		2.7%			

The elements marked * are in general of major significance. The others, even though occurring in major quantities are not so troublesome in the respect that they either make small contribution to the radioactivity or are gaseous.

In addition, the charge will contain breeder products uranium-233

and plutonium, unutilised fissile material and intermediate regenerative products leading to breeding as shown below :—

$$Th^{232} \xrightarrow{n,\gamma} Th^{233} \xrightarrow[23.5\ min]{\beta} Pa^{233} \xrightarrow[27.4d]{\beta} U^{233}$$

$$U^{238} \xrightarrow{n,\gamma} U^{239} \xrightarrow[23.5\ min]{\beta} Np^{239} \xrightarrow[2.3d]{\beta} Pu^{239}$$

The composition of spent fuel from a natural uranium reactor which has operated for one year at a power level of 28 megawatts, will roughly be uranium (all isotopes) 99.954 percent, plutonium 0.023 percent and fission products 0.023 percent.[8]

Radioactivity of the charge

The charge for reprocessing emerging from the reactors is highly radioactive, the actual amount being dependent, other things being equal, on the extent of irradiation undergone.

The influence of radioctivity in reprocessing programmes generally arises from the chemical effects and health hazards associated with it. These combined together constitute important and often decisive considerations in planning and selection of the entire approach. They will now be examined briefly within the scope of paper stated above. The action on dielectric materials of high energy electrons present in the charge causing considerable changes in their electrical, mechanical and optical properties should also be pointed out here. Interesting studies on the subject have been recently reported by Gross for borosilicate glass[9].

Nature of chemical effects of radioactivity

The extent of effects produced will be determined by the nature and concentration of radioactivity and length of exposure. As a general rule[10a] it may be mentioned that β activity generally produces more chemical change than γ. β activity is almost totally absorbed in process materials in contrast to γ. It is this penetrating γ radiation, that requires heavy shielding for its confinement. Damage from α radiation is similar to β, though more intense. In all the three types of radiations, chemical change takes place through the excitation and ionisation of molecules. However, while radiation provides energy and local oxidising and reducing effects, these effects cancel unless a more stable form results in one direction than in the other or unless the reaction is irreversible. This points to the vulnerability of organic compounds where bonds broken will generally not reform. Hydrolysable compounds and aqueous solutions, where stable gas phase can exist on molecular disruption are also likely to be affected. The formation of gas could in turn alter the course of equilibria if some volatile products or re-agents are involved.

Another category of substances whose chemical behaviour is liable to considerable modification in presence of radiations will be those involving polyvalent radicals. The importance of this particular factor will be apparent when it is realised that uranium, plutonium and many accompanying contaminants are polyvalent in character and in separations based on distribution of the elements into two mechanically separable phases, reactions involving the change of valencies offer the most effective control in achieving selectivity. In dilute solutions, most of the energy is absorbed by the solvent and the primary products formed are characteristic of the solvent rather than solute.

Consideration of chemical effects of radioactivity in determining the processing cycle, materials of construction and equipment

The nature of chemical effects associated with the radioactivity has been explained above. It has to be repeated that these generally become perceptible above certain levels of radioactivity, their intensity increasing with increase in activity of the charge. Though in the discussion below, the levels of radioactivity at which some of these actions assume perceptible proportions have been indicated in a broad way, it has not been possible to do so for all the individual factors in a generalised presentation like this.

Relative instability of organic compounds and susceptibility to modification in the usual chemical behaviour of polyvalent, elements in the presence of radiations for reasons explained above, imply that in the charge which has not decayed sufficiently, any scheme involving organic reagents or materials and adopting aqueous methods of separation based on change of valency is less likely to succeed. The best organic complexing materials can be exposed to only 0.00001 watt-hours per gram[4]. They would usually break to give off hydrogen and usaturated compounds. Ion exchange resins also get subjected to damage as reflected by loss in their capacity, swelling behaviour and selectivity towards various ions. Anion resins have less radiation stability than cation resins. Among resins, sulphonated phenolic resins have proved to be the most stable to radiation.

The above would explain reason for the practice in such cases of allowing the charge to "cool" for a period of months to allow the radioactivity to decay to convenient levels. Further relief is obtained by diluting the solutions before treatment. Inorganic reagents are expected to be more stable at the same levels. Similarly, usual insulation used on electrical wires which has organic ingredients in it may have to be replaced for example, by metallic sheathed cables insulated with silicone impregnated mica or some other mineral insulation. Resistance heating might assert itself for working in intense radiations against induction heating, which was previously considered to be superior because of the difficulties involved in cooling the coils[11]. Hydrogenous materials like water as coolants would not be stable

enough and use of sodium-potassium alloy required for the purpose is found to result in a complex and costly cooling system. Teflon, polymerised tetrafluoroethylene, normally an excellent material for gaskets, becomes brittle and decomposes to give fluorine, leading in turn to severe corrosion problems[5].

Ordinary plate glass undergoes discolouration on exposure and has to be stabilised by suitable additions. Existing types of stainless steel were not considered to be resistant enough or stable enough in the presence of radiation to be suitable and new ones had to be developed[12]

Again when working in intense radioactive fields, the tendency for the gaseous products to form puts the precipitating techniques into disfavour, because the mechanical and thermal effects associated with gas generation lead to peptisation of the precipitate, making the separations difficult. Methods based on electrodeposition would lose part of their advantage due to difficulty of obtaining compact deposits and good current efficiency in presence of gas evolution. In ion exchange columns, the formation of gas bubbles will tend to plug the column.

Last but not least, the reactions selected for processing must yield high material efficiencies because of the toxicity, high cost and scarcity of materials being processed. Particularly in the treatment of breeder blankets, losses in the recovery and purification of uranium-233 and plutonium right upto the stage of reduction back to their metallic state must be less than a few per cent since otherwise any small gain in the pile will go down the drain. Uranium and plutonium must often be separated from each other by a factor of ten thousand and from as many as 35 fission products by a factor of ten million and recovered with a yield in excess of 99 per cent.

In the design of assemblies, besides pure chemical engineering considerations there is an additional consideration of the geometrical form and dimensions of the entire assembly because in no cross section, concentration of fissile material should exceed the amount required for it to reach criticality : a substantial problem when considered that in a plant processing plutonium on scale of 50-100 Kg. per day, less than one-tenth of the quantity dissolved in water could serve as a critical reactor[13].

Considerations of health hazards of radioactivity in the determination of processing scheme and equipment

Health hazards resulting from exposure to radioactivity dictate the use of shields, many feet thick. The shields are required when exposure at handling distances is likely to exceed the tolerance level of 7.5 mr/hour.[14] Processing under such circumstances will have to involve such techniques, unit operations and equipment that could

readily lend themselves to remote control and demand for their components least maintenance, repair work and replacement because in the circumstances these will be complicated, involved and expensive if not really impossible. Direct maintenance plants, if are to be used, must incorporate only such equipment which could admit easy decontamination. Flanged joints, glands or pumps requiring packings or gaskets or electrical contacts are looked upon with suspicion. Welded joints are usually preferred to flanges. Components with moving parts, because they require application of lubricants and occasional attention are also avoided for circulation of fluids. Instead of conventionally employed valves, use is made instead of unit operations like vacuum transfer, gravity flow, gas lifting and blocking the U-shaped bends in pipes where required by freezing the liquids etc. For transfer of some liquid metals, pressure of silver vapour—"vapour pump"—is being employed. Electro-magnetic pumps are being increasingly used. For separation of solids, there is general tendency to adopt centrifugation instead of filtration, because of the difficulties inherent in the latter for setting up and cleaning the filters and handling the separated solids by remote control. Powder metallurgy could be of great assistance in this field by developing metallic media such as sintered stainless steel and platinum which are likely to reduce some of these difficulties associated with filtration. For centrifugation when working at high radiation intensities and there is chance of gas evolution, bowl type of centrifuges are preferred which would allow continuous overflow or skimming of the liquid phase while spinning at full speed.

For electrical systems in high intensity radiations, Basel and Koslov have recently given some of the considerations.[11] Totally enclosed fan-cooled type of motors with class H insulation provide maximum reliability and minimum maintenance. Use of insulation based on inorganic ingredients has already been mentioned. Motors and heaters are wired by means of "connectors" and jumpers which can be removed and installed by the manipulator.

While examining the implications arising from the health hazards, mention should also be made of the consideration of radio-active effluents. Storing of these till the radioactivity has decayed presents problems of quite a magnitude. If large quantities of these result from a particular mode of processing, it is considered a positive disadvantage of the process and supplementary step of evaporation to effect reduction in volume has to be incorporated. Ion exchange techniques have also been used for reducing volumes. It is also this consideration that weighs against precipitation techniques and unit operation of filtration, both of which involve considerable wash liquors. Distillation, sublimation and fusion separations will be ideal from this point of view.

Separation Processes

Reprocessing is undertaken as explained earlier for one or more of the following purposes :

(i) Removal of the poisoning elements (parasitic neutron absorption).

(ii) Reduction of the activity of the charge to facilitate handling and fabrication without heavy shielding.

(iii) Recovery of fission material in a form suitable for use.

(i) *Poisoning* :—Excepting xenon, most of the poisoning to be reckoned is in the rare earths, samarium, gadolinium, neodymium, europium and in iodine. The next group of fission products in order of decreasing importance as poisons are cadmium, strontium, cesium, rhodium and krypton[15]. The extent to which the classes of fission products are significant after long burn up will be evident from table II given below :

Table II : Contribution of various constituents to total Neutron Poisoning (poisoning due to Xenon-135 has not been counted in the total).

Rare earth metals	App.	65	percent
Caesium and strontium	App.	10	,,
Xenon & krypton	App.	15	,,
Rhodium & cadmium	App.	10	,,

The emphasis to be put on the removal of these will depend on the type of reactor required to be served. For example, poisoning would not be of much consequence in fast reactors where not much absorption of neutrons is to be feared, but in a thermal reactor where any loss of neutrons is to be scrupulously guarded against it would be of paramount importance and highest degree of separation of poisoning elements may be called for.

(ii) *Reduction of activity* : Besides gases, the activity in charges rests mainly with cesium, strontium, promethium and rare earths. Its reduction is sought to facilitate chemical operations and mechanical fabrication without shielding. But if the design of fuel element is simple and it can lend itself to fabrication by remote control without excessive difficulties, stress on this factor will be relatively minor. In the case of fuel elements of complicated design, however, costs involved in fabrication by remote control will be prohibitive, leading to an entirely different situation.

The most persistent troube-making elements in this respect are zirconium, strontium and ruthenium.

(iii) Suitability of fuel implies both nuclear and metallurgical considerations. Nuclear considerations will be determined by the use to which fuel has to be put. In case of plutonium recovery, for ex-

ample, plutonium-240 content is undesirable in the metal required for armaments and its complete removal is desired. The consideration of poisoning has already been pointed out before. With respect to metallurgical considerations, the metal should be free of inclusions that would distort the lattice of metal excessively or lead to serious corrosion problems. The metal or alloy on fabrication is required to yield most resistent microstructure on which factor the radiation damage generally depends. Though at the present stage of experimental work, it is not possible to establish the individual effects, as a general rule it may be stated that a non-metal like xenon or a large atom like cesium would tend to impair rather than improve matters. Considerations of atomic radii of metals may serve as guide in this respect, though too much reliance on them at this stage may not be safe enough. Rare earths in small concentrations may not be really harmful and fission products ruthenium, niobium and molybdenum at low concentrations might be actually useful,[15] in which case it may not be necessary to remove them as long as they do not interfere with any other consideration. Studies along these lines on the reaction of lattices of nuclear metals to additions in small amounts of many elements very uniformly dispersed are urgently needed. These will involve some of the most complex alloy systems the like of which in complexity have not been encountered before in metallurgy.

Practice of Reprocessing

It is not intended to give here the details of various practices. The scope will be confined to indicating the nature of reactions employed for effecting various separations and their general outline. The practices may be broadly classified as (i) Aqueous techniques and (ii) Pyrometallurgical and high temperature techniques.

Aqueous techniques : Included are (i) solvent extraction (ii) ion exchange and (iii) precipitation. The attention will, however, be mainly confined to the solvent extraction method which appears to be almost universally used for large scale treatment of irradiated materials.

Solvent extraction method: *Current industrial practice* : It is based on the solubility of nitrates of heavy metals i.e. uranium and plutonium in oxygenated organic solvents, allowing easy removal of rare earths. In some cases, the extraction is through the formation of well defined co-ordinated complexes. The extractability is dependent on extent of nitrate complex formation and all the separations are based on playing up with the complex forming tendencies of various constituents through additions of salting agents and varying of acid concentration etc.

The solvent generally used is n-tributyl phosphate diluted with some inert addition like kerosene oil. Dilution is necessary, because otherwise viscosity of the liquid will be inconveniently high. Some of the

other extractants that have been used are: pentaether, di-isopropyl ether, tertiary alcohols, thionyl trifluoroacetone and dibutyl carbitol. Based as these methods are on organic and aqueous materials, they entail a "cooling" period of 3-4 months or even more, so that radioactivity decayed to convenient levels. The damage on tributyl phosphate will be perceptible at radioactivity equivalent to 0.5 watt—hr/litre[10]. It decomposes and hydrolyses to give hydrogen and unsaturated organic compounds.

For uranium based charge, general cycle consists of dissolving the "cooled" irradiated charges to give nitrates, recovering the metals uranium and plutonium together from other fission products in the first instance and then effect the separations between themselves. In effecting dissolution, nitrogen oxide fumes produced from nitric acid are recovered by oxidising. Stainless steel is the material generally used for equipment.

In the separation of uranium and plutonium from fission products by solvent extraction, uranium and plutonium have to be maintained in the hexavalent and quadravalent states because it is only in that state they are soluble in the solvent. The addition of salting agents (aluminium nitrate in case of aluminium clad uranium fuel) and control on hydrogen ion concentration is important.

For separation of uranium from plutonium, advantage is taken of the fact that plutonium when reduced to trivalent state is no longer soluble in the organic solvent. Uranium is still active enough to prevent the fabrication without shielding. Further purification is necessary to remove this residual activity.

In the case of irradiated thorium, to facilitate dissolution, fluoride ions are added to nitric acid to serve as catalyst. They probably serve to remove the oxide film formed on thorium in the presence of nitric acid.

Before submitting to solvent extraction, solution of the charge is some time passed over manganese dioxide to remove bulk of protactinium with which about 95 percent of activity is associated.

The separation of thorium from uranium-233 produced is not as easy as in the case of uranium and plutonium, because thorium is not readily extractable and reliance has to be put on the differences in extrability of thorium, uranium and fission products under different conditions. Dibutyl carbitol and tributyl phosphate have been successfully used, the former under acid deficient conditions and latter in acid media[7]. Thorium thus separated may still contain some zirconium and protactinium. Separation from these is often effected by absorption on either silica gel or activated charcoal. Uranium-233 may be concentrated and purified by ion exchange.

The most difficult element to handle in solvent extraction is ruthenium. Plutonium and uranium recoveries are based on the basis of oxidation exchanges and since ruthenium also readily changes its oxidation state, its separation becomes difficult. Ruthenium solutions easily get reduced to the metal state and metal deposits on solid surfaces. The tendency of its compounds to hydrolyse leads to the formation of colloidal solutions. Among the other more difficult separations are zirconium and niobium. Iodine is also a source of considerable trouble.

The outstanding advantage of the solvent extraction process is in its flexibility. Solvent extraction technology has progressed to the point that any of the fissile and fertile material can be separated from each other, from fission products and from inactive diluents and contaminants. Its weakness lies in its sensitivity to radiation. All the same, this process is not likely to be changed in the near future, though it should be read in the context of what follows in the latter part of the paper.

Ion exchange processes : They have not yet played sufficient role. In general they have same advantages and disadvantages as solvent extraction. They can be made highly specific for the removal of substances in very small concentrations. Consequently they have been used for recovering uranium from scrub liquors and concentrating radioactive products from large mass of wash liquor and effluents. Ion exchange methods offer means to effect separation amongst constituents of same valency and should be better suited to work in higher intensities. The principal developments required are in the production of radiation stable (inorganic?) exchangers.

Precipitation processes : They are not popular at present but may find application where quickprocessing and reconstitution of nuclear fuel are desired. Likely ones are precipitation of uranium and plutonium peroxide, plutonium and thorium oxalates and plutonium fluoride.

Pyrometallurgical and high temperature techniques

Pyrometallurgical processes are intrinsically simple and treat the charge in molten state, using for the separations inorganic extractions or reaction media. Gases, iodine and a high proportion of the other contaminants like cesium, strontium having appreciable vapour pressure at higher temperature are removed automatically during melting. For the remaining elements, resort is taken to the following general techniques: (i) Extraction with liquid metals (ii) Extraction with fused salts (iii) Zone refining (iv) Slagging with oxides (v) Selective chlorination or fluorination of the components.

The above would not be gone into here because they form the subject matter of a subsequent paper. Pyroprocessing is characterised by the fact that "cooling" of the charge can be practically eliminated due to the absence of radiation sensitive media. The charge from re-

actor has considerable heat content in it to facilitate melting. It is straightforward in the respect that no dissolution and consequent recovery of the materials from aqueous solutions to be converted back to pure anhydrous compounds for subsequent reduction to the metal state is involved. Radioactive effluents and wastes are thereby reduced to very small quantities.

Main disadvantage at the present stage of its development is lower degree of decontamination attainable. Hence metallurgical fabrication of the recovered product has to be done behind shielding under remote control.

Philosophy of Reprocessing Programmes

Now that the general outline of the current practice has been presented and alternate approaches briefly touched upon, it may be useful to state the general philosophy involved in these programmes of processing. Whereas the general desire is to keep the processing in highly active environments to a minimum, any effort in that direction has to be considered in the context of urgency of keeping the reprocessing cycle as short as possible. One way could be to determine the elements with which the major part of radioactivity is associated—in a charge of irradiated thorium for example, 95 percent of radio-activity is associated with protactinium-233—and proceed to remove them as early as possible so that the rest of processing could be carried out under less adverse conditions. Heavy shielding is necessitated by prevalence of high activity and to keep the working behind such shielding to minimum, premium is put on an early elimination of emitting substances. Special attention is also paid to the elimination of highly active gaseous and volatile products, xenon and iodine, because they are so liable to escape into atmosphere bringing in their wake serious atmospheric pollutions. The elements whose isotopes are either of very short life or considerably long life or which emit weak β radiations are not a bother as far as their radioactivity is concerned.

Next is the consideration of flexibility which will be very important for the next 10-15 years till sufficient information has been collected from the reactors of various designs now being investigated to enable more definite conclusions to be drawn about the types of reactors which are likely to prove popular eventually. Here purely scientific considerations will get mixed up with political considerations which could be very weighty. For instance, the recent increase in price of plutonium, material required for nuclear armaments, from \$12|- gram to \$30-45 per gram[2], is bound to have influence on reactors designed for power generation in the respect, that in the designs there will be greater accent on breeding of by-product plutonium than before. Since the capital costs involved in setting up reprocessing plants are high, there will be natural temptation to adopt a particular processing which can handle a variety of fuels in preference to another which may be superior for the particular job but not possessing that flexibility. This explains

why the statistics about different processes being employed in the various plants cannot be taken at their face value to gain an idea about the superiority of one over the other for the particular job being carried out at that plant. Further in examining the apparently preferred practices, it is important to bear in mind that the first plutonium recovering plant in U.K. was based on the experience which consisted of handling only a few milligrams of plutonium. While building up facilities for the processing of such a dangerous metal on the basis of experience so meagre about its nature, it should be expected that the consideration of safety and reliability was naturally paramount, reflecting in the tendency to adopt only such operations with which the chemical industry has had long experience and feared least complication. Extraction techniques involving aqueous liquid phases offered such promise, because circulation and control problems in their cases at the temperatures involved are relatively simpler. On account of the high toxicity of materials and associated risks mentioned above, any attempt at change until absolutely necessary or forced upon, is, therefore, bound to meet with considerable resistance. In the circumstances, there is liable to be a strong desire to improve on the existing ones on the basis of experience gained rather than adopting an entirely new approach. Thus the current industrial processing practice is not likely to be replaced in the plants being erected or planned for the next few years. Alternate methods based on pyrometallurgical techniques should be considered on their merits and in as much as they promise to cut down substantially the period of recycling and possess the criterion of straightforwardness they are most likely to assert for themselves a place in industrial operations as the reactor designs get standardised.

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Discussions

Mr. S. Sen, (*Atomic Energy Establishment, Trombay*); In addition to the solvents mentioned by Mr. Manocha for processing irradiated fuel elements, I would like to mention that M.I.B.K. (hexone) is also used industrially as a solvent under acid-deficient conditions for extraction of uranium and plutonium. As an example of industrial use I might mention the Idaho Chemical processing plant which processes the irradiated fuel elements of the M.T.R. and B.S.R.

In connection with dilution of T.B.P. I would like to add that the dilution of T.B.P. is necessary not only to reduce the viscosity as mentioned by Mr. Manocha but also to reduce the density, surface tension and distribution co-efficient as well as to increase the separation factor with respect to the impurities. Reduced density means higher density difference, i.e. higher flooding velocity, so that the equipment can be run at a higher capacity. Decreased surface tension, increases the rate of transfer and thus requires a shorter column for a given separation. The reduction of distribution co-efficient is sometimes necessary to make stripping feasible. The exact degree of dilution is governed by the factors discussed above.

"Burn up of 1% introduces 2% impurities".

I would like Mr. Manocha to explain the above.

Author's Reply : It is burn-up of 1% of atoms—the percentage is expressed as atomic percent.

Dr. T. R. Scott, (*Australia*): The price of plutonium has also been reported to be $. 15 to 18 a gram. In this paper it is mentioned $. 30-45 per gram. What is the reason for this discrepancy?

Author's Reply : The price of $. 15-18 per gram is the older price. It has been recently increased according to an announcement by U.S. A.E.C., to the price mentioned in the paper i.e. $. 30-45 per gram. The exact price in the range of $. 30-45 is determined by plutonium-240 content in plutonium-239. Plutonium-240 content is considered undesirable in armament applications. The maximum permissible Pu-240 content is about 6 percent.

RECENT DEVELOPMENTS IN THE PYROMETALLURGICAL TREATMENT OF IRRADIATED FUEL ELEMENTS AND BREEDER BLANKET IN THE U.S.A.

*By Stephen Lawroski**

ABSTRACT

Intensive study is being continued in the United States on the pyrometallurgical treatment of irradiated fuel elements and breeder blanket. Metallurgical properties and irradiation behavior are being investigated on metal alloys corresponding in compositions to those obtaining from recycle operations by pyrometallurgical processing. Since this type of treatment results in only partial removal of fission products, parallel studies are in progress on procedures and equipment for remote fabrication of fuel elements. Encouraging results have been realized in each of the aforementioned development areas. In at least one case the decision has already been made to design, construct and operate a pyrometallurgical processing plant in conjunction with a fast reactor project.

Interest in pyrometallurgical methods of processing irradiated fuel elements and breeder blanket has been stimulated in the United States by the necessity for developing low-cost fuel cycles in order to achieve nuclear power at costs competitive with those of conventional fossil fuel sources. At the present time all fuel and blanket reprocessing is being done by solvent extraction methods employing aqueous-organic systems. These methods have proved effective from the standpoint of thorough purification and essentially complete recovery of products. However, their costs are very substantial. Much of the total cost stems from the need of chemical conversions before and after processing. These conversions result in large volumes of process and waste solutions as well as in a large number of operating steps in the over-all fuel cycle. Hence, the plants are large and expensive. In addition, these methods require substantial duration of fuel storage before start of processing. This is done to alleviate radiation damage to solvent. As a consequence, very large inventories of fissionable material are accumulated. A significant example of this was recently reported (October, 1957 meeting of Atomic Industrial Forum in New York City) for the fast breeder-power reactor being built near Detroit. It was estimated that the total inventory will amount to over 1000 kilograms of enriched uranium valued at approximately $15,000,000. Approximately two-thirds of this inventory occurs outside the reactor. At appropriate interest charges, the inventory charges alone contribute 1 to 2 mills per kilowatt hour of electrical power produced.

The factors cited illustrate some of the economic disadvantages of processing power reactor fuels by aqueous solvent extraction methods.

* Argonne National Laboratory, Lemont, Illinois. Prepared for presentation at Symposium on Rare Metals, The Indian Institute of Metals, Bombay, India December, 1957.

Some improvement in this situation is possible. At present it appears that the improvement must depend to a large extent on the use of large central plants wherein large rates of processing will help to reduce unit costs. At the same time it may be possible to improve the inventory situation particularly if there are several reactors which use identical type fuels. Even with these potential improvements it is still not certain that the aqueous solvent extraction processes will be adequately economic for all processing purposes. Therefore, serious consideration has been given to pyrometallurgical processes with the results that their development has been very actively undertaken. Although these processes may be applicable to thermal as well as fast reactor fuels, it appears that their potential advantages over conventional solvent extraction processes are greater for fast reactor fuels. Some of the reasons for this conclusion are as follows.

Insofar as it is now known, the poisoning effect of residual fission products is less for fast reactors than for thermal reactors. Therefore, it does not appear necessary to remove thoroughly all the fission products when reprocessing fast reactor fuels. Repair of irradiation damage might be the principal purpose of reprocessing. It is believed that pyrometallurgical methods can accomplish this and an adequate removal of fission products. Fuels for fast reactors must be of relatively high fissionable material concentration in order to achieve and maintain criticality. Moreover, substantial dilution with alloying agents, such as is frequently practiced in thermal reactors to enable large fractions of fissionable constituents to be fissioned, results in large penalties in fast reactors as regards critical mass increases. The overall consequence of these factors is to impose on fast reactor fuel recycle severe problems as regards inventory of fissionable material and high frequency of fuel reprocessing. Therefore, undelayed processing and low unit costs are especially important to fast reactor fuels. Because most of the envisioned pyrometallurgical processes do not require chemical conversions and do not suffer serious radiation damage problems, they appear advantageous for minimizing fissionable material inventory and unit processing costs. Although they do not completely remove fission products, these processes are believed capable of providing purification sufficient for repair of radiation damage and restoration of reactivity in fast reactor cores. The problem of blanket processing is primarily one of enriching the concentration of fissionable content to a value suitable for use in replenishing the material consumed in the core. It is believed that, again, one or more of the pyrometallurgical methods will serve the purpose.

Pyrometallurgical Treatments

Some work has been done on pyrometallurgical methods such as zone melting, fractional distillation and electrochemical treatments. Except for the last one, the results on these have been limited and unencouraging. Zone melting appears to be impracticably slow as regards rate of processing; fractional distillation, e.g., to separate plutonium and uranium metals, poses unusually difficult problems of materials

of construction because of the extremely high temperature of operation for long durations. The pyrometallurgical methods which have been considerably more promising and on which development studies have been emphasized are oxidative drossing and intermetallic crystallizations from metal solvents for core purification and molten metal solvent extractions with magnesium for blanket processing.

For purposes of core processing the most extensively studied pyrometallurgical treatment has been oxidative drossing.[1, 2, 3] In practice this treatment of melting a fuel charge and maintaining it as a liquid for 3 to 5 hours at 1200 to 1400°C and making a provision for a limited supply of oxidizing medium. After this period the dross and the purified metal are physically separated by pouring away the latter. Perhaps a more appropriate name for this method of treatment is "melt refining" because an appreciable fraction of the total purification occurs simply by the volatilization of several fission products when the fuel is melted. The principal fission products removed by this mechanism are krypton, xenon and cesium. The remainder of the purification during oxidative drossing results by selective oxidation of those fission products whose oxidized compounds are more thermodynamically stable than those of uranium. An examination of the illustrative information given in Table 1 shows that strontium and the rare earths yield oxides

Table 1 : Free energy of formation of oxides, Kilocalories per Gram-Atom of Oxygen

(Data from reference 4)

Compound	$-\Delta F°$ at 298°K	1000°K	1500°K	2000°K
ThO_2	140	125.5	115.0	104.5
CaO	143	131	114	99.3
La_2O_3	136	123.3	112	100.3
BeO	136	123.3	111.6	99.5
Ce_2O_3	137	120.3	107	94
Pr_2O_3	140	120	106.7	94.3
MgO	136	119	103	78.9
Al_2O_3	126	112	102	93
SrO	134	116	102	80.4
UO_2	123	109	99	88.5
ZrO_2	124	108	97	86.5
Li_2O	134	112	96.1	66.0
BaO	126.5	111	95	80
PuO_2	117	100	95	85
SiO_2	98	82.5	72	61
NbO	89	76	66	57
CO	33	47.9	58.4	68.5
H_2O	57	46.0	39.3	32.3
MoO_2	122	46.5	38	30
TeO_2	32	15.8	4.7	—7.3
Cs_2O	65	35.1	3.6	—15.7
RuO_2	22	6.0	—2.7	—10

which are more stable at 1500°K than uranium or plutonium oxides.[4] Consequently, these fission products would be expected to be separable from uranium or plutonium by controlled oxidation with oxygen at 1500°K. On the other hand, the data in Table 1 show that thorium could not be similarly purified from these fission product elements. From this table it can also be anticipated that oxide drossing of irradiated uranium or uranium-plutonium would give little or no purification from niobium, molybdenum and the noble metals, e.g., ruthenium.

As the result of demonstrated convenience and effectiveness, the oxidative drossing technology has emphasized the oxide system and the use of an oxide crucible itself as the source of oxygen for the controlled selective oxidation. The principal variables whose effects on purification and recovery have been investigated in connection with this pyrometallurgical method of core processing have included fission product element concentrations, batch size, temperature, time, crucible material and process atmosphere.

Fission product element concentrations have been studied over a several hundred-fold range. They have included values corresponding to mildly irradiated uranium or uranium-plutonium up to values corresponding to large burn-ups of these fuels. The studies on the latter have been made with the aid of inactive fission product elements added to unirradiated or midly irradiated uranium. It has been found that the amount of purification and recovery is nearly independent of the concentration level of fission products. Typical fission product removals effected experimentally by oxide drossing operations in ceramic oxide crucibles are given in Table 2. Experiments on oxide drossing

Table 2: Fission Product Removals effected in Oxide Drossing operations

Greater than 90% Removed	40–90% Removed	0–10% Removed
Rare Earths	Zirconium	Niobium
Yttrium*	Tellurium	Molybdenum
Strontium	Cesium	Technetium*
Xenon*		Ruthenium
Krypton*		Rhodium
		Palladium

* No quantitative experimental data, but indicated result seems very probable.

have been made on charge sizes from approximately 200 grams to 5 kilograms. As might be expected, larger recovery is possible with increased batch sizes. The effect of batch size on purification is not large. The somewhat slower rates of purification obtaining with larger batches and with larger impurity concentrations can be compensated by employment of slightly higher operating temperatures to increase the rates

of oxide reactions. The effects of temperature variation from 1200 to 1400°C and of liquation time from 1 to 5 hours duration have also been studied. The influence upon product recovery and impurity removal in oxide drossing has been studied as a function of the composition and method of manufacture of crucible employed.

As implied by Table 3, many of the variables studies have usually been conducted with the use of cerium in uranium to determine process

Table 3 : Determination of Cerium removal under various operating Conditions

(Charge size of fuel—approximately 2 kilograms unless otherwise noted)

Reference Run	Liquation Temp. (°C)	Crucible	Liquation Time (Hours)	Product Yield (%, cerium-free basis)	% of Original Cerium Removed
1	1200	Pressed ZrO_2	3	96.1	59.3
2	1300	Slip-cast MgO	3	95.2	Nearly 100
3	1300	„ „ „	5	90.8 (a)	75.7
4	1300	Pressed MgO	3	97 5	72.2
5	1300	„ „	3	94.2	—
6	1300	„ „	5	94.7	64.3
7	1300	Pressed ZrO_2	3	97.1	92.0
8	1300	„ „	3	97.7	—
9	1300	„ „	5	97.3	99.6
10	1300	„ „	5	96 3	98 9
11	1300	„ „	5	94.5	89 5
12	1400	„ „	2	93.6	90.4
13	1400	„ „	3	94.6	97.6
14	1400	„ „	3	93.0	Nearly 100
15 (b)	1300	Pressed ZrO_2	5	95.1 (b)	(b)
16 (b)	1400	„ „	2	95.0 (b)	(b)
17 (b)	1400	„ „	1	95.4 (b)	(b)

(a) Part of product lost by spill

(b) Runs 15, 16 and 17 made with 5476, 5142 and 3000 grams, respectively; these runs were made primarily for yield reproducibility.

effects. The choice of cerium is made because it is conveniently available and because its behavior in oxide drossing would be expected, according to the information given in Table 1, to be similar to that of the whole rare earths group. The concentration of cerium is adjusted to correspond to the amount of cerium plus the rare earths in highly irradiated fuel. From various data, some of which are shown in Table 3, it appears that the use of pressed zirconia crucibles and liquation times of about 3 to 5 hours at temperatures of approximately 1300°C will be satisfactory for eliminating at least 90% of the fission products capable of removal by oxide drossing. Shorter liquation time might be possible with higher temperatures but this advantage is small and may be even obviated by the need of close temperature control to avoid excessive oxidation with resultant loss of product yield. Product yields of the order of 95 percent or better can be reasonably expected. As

much as three-fourths of the remaining 5 percent is metal loss by occlusion in the oxide dross. Recovery of this appears possible by the Pyrozinc process which will be later discussed. Heating to and maintaining operating temperatures for oxide drossing operations have been found to be conveniently and reliably possible by induction methods (10,000 cycles). Of the various crucible materials tested, which have included alumina, magnesia, thoria, urania, zirconia, beryllia, oxide-coated graphite and others, it appears that dry-pressed zirconia is preferable and would be recommended at this time. This choice is based on considerations of thermal shock resistance, low corrosion rates by liquid metal, negligible contamination of purified ingot, reproducibility of yield and fission product removal, and availability at moderate cost. It is interesting to note that magnesia was once considered seriously. However, it was subequently found that the evolved magnesium metal vapor disturbed the liquation of oxide dross particularly in larger scale experiments.

As can be noted from the right-hand column of Table 2, oxide drossing fails to remove a substantial number of fission products. The concentration of these will increase upon continued fuel recycle by this method of processing. The final concentrations attained can be controlled and will depend on the fission product spectrum, process efficiency and, primarily, on the fraction of new fuel material added per cycle. To avoid dealing with fuel of continually changing composition, it seems preferable to start with a fuel whose initial composition corresponds to the equilibrium concentration for a fixed amount of old fuel "dragged out" in each cycle and replaced by new and essentially pure fissionable material. At present it appears from oxide drossing experiments that this fraction of "drag-out" should be between about 5 and 10 weight per cent of the total fuel. With the assumption of this type of operation, calculations have been made for determining the equilibrium fission product concentrations in a fuel as functions of the particular isotope fissioned, of the degree of fission product removal and of the fraction of old fuel dragged out per cycle. For convenience, the term "fissium" (symbol-Fs) is frequently used in referring to such compositions; e.g., uranium-fissium alloys. Since the effects of these residual fission products on metallurgical properties and irradiation behaviour of "fissium" fuels are most important in any consideration of this type of reprocessing, certain uranium base and uranium-plutonium base alloys have been prepared with the calculated equilibrium fission product concentrations. To date the results of studies on the metallurgical properties and the irradiation behavior of these compositions have been very encouraging.[5,6] Thus it appears that there may be some distinct advantages to the limited removal of fission products as obtained by oxide drossing. In conventional processing the use of such alloys or related compositions serves only to complicate the processing by giving rise to problems of initial aqueous dissolution and final waste disposal operations.

It has been mentioned earlier in connection with product yield during oxide dross operation that a significant fuel loss occurs as metal occlu-

ded in the dross. Subsequently it was also pointed out that some amount of fuel removal or "drag-out" is necessary to limit the build-up of certain fission products which are not eliminated adequately by oxide drossing. In both of these instances it is necessary to incorporate some provision for the recovery of contained fissionable material. The use of aqueous methods, for this purpose only, would be expensive and would largely negate the original use of pyrometallurgical treatment. Therefore, a pyrometallurgical type process has been sought to accommodate this recovery operation. It is believed that a variation of the Pyrozinc process which is being developed at Argonne will be suitable. In this process[7] the difference in the solubility of various metals in molten zinc (see Figure 1) may be used to enable separation of uranium and plutonium from fission products. To date only preliminary but favorable results are available on the use of zinc with about 5 weight per cent magnesium to recover uranium from oxide drosses and "drag-out" fractions. The uranium is recovered in the form of UZn_9 crystals. At temperatures of about 950°C this compound can be decomposed and the zinc eliminated. The resulting uranium powder can be agglomerated into massive metal by briefly heating it to temperatures above the melting point of uranium. By use of this procedure, satisfactory metal has been recovered with a zinc content of about 30 ppm.

In connection with studies of the use of zinc-magnesium metal on oxide drosses it has been found possible to separate the occluded metal from the oxide. In addition, under certain conditions it is possible to reduce oxidized uranium to metal with this mixture. This may be very significant since it suggests a route for reprocessing of oxide fuels by pyrometallurgical treatment.

In addition to the above-mentioned processes, the use of zinc[7] and mercury[8] for overall reprocessing of reactor fuels is also under study. Another very promising high temperature method of recovery process is an electrochemical method[9, 10]. This method may be employable for metallic and oxide fuels. At the present time this is perhaps the most encouraging method for reprocessing the latter type of fuels by pyrometallurgical treatment. A fused salt extraction process is being developed for the Liquid Metal Fuel Reactor[11] at Brookhaven National Laboratory in which the fuel is uranium dissolved in bismuth[1, 2].

The various pyrometallurgical treatments which may be used on reactor core processing have been discussed above. Simultaneously, some attention has also been given to processing of blanket material by pyrometallurgical methods. In this instance, the recovery or concentration of plutonium has been worked on by the use of liquid-liquid extraction of molten uranium by fused salts or molten metals[1, 2]. The most thoroughly studied of these to date has been an extraction with molten magnesium. With equipment built of tantalum, studies have been conducted up to multi-kilogram scale of uranium with plutonium concentrations ranging to at least 1 weight per cent[2-12]. A variation of this process has been the use of liquid magnesium to leach plutonium

as a Function of Temperature

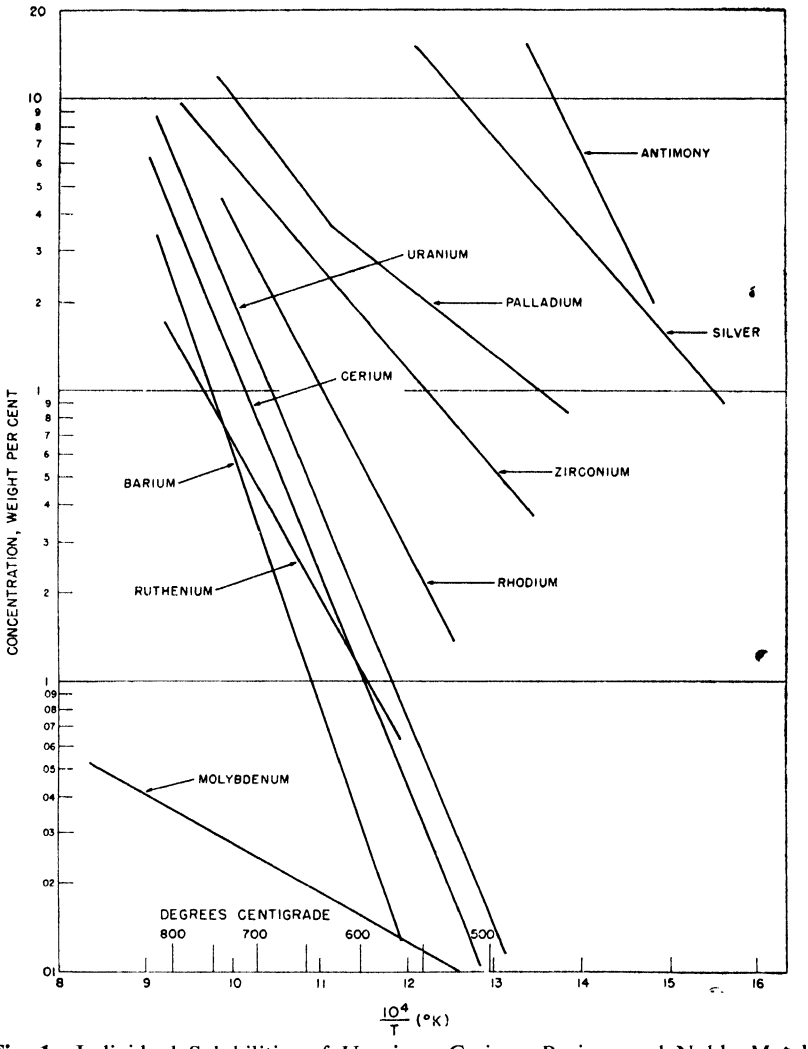

Fig. 1—Individual Solubilities of Uranium, Cerium, Barium and Noble Metal Fission Product Elements in Zinc as a Function of Temperature

from solid uranium powders obtained by hydriding and dehydriding[13]. Other work on pyrometallurgical blanket processing has been on the separation of uranium from thorium[1] but this work is at a very preliminary stage.

Remote Fuel Fabrication

Inasmuch as the pyrometallurgical processes recover the product only partially decontaminated from fission products, it will be necessary to

develop remote fabrication techniques. The need for some form of remote fabrication may exist even for fuels which are completely freed of fission products because the product may still be radioactive from the build-up of heavy isotopes. Remote fuel fabrication has been very actively undertaken in connection with the Experimental Fast Breeder Reactor Project. In this instance the fuel is in the form of rods approximately 14 inches in length and $\frac{1}{8}$ inch in diameter. It appears that an injection casting procedure (see Figure 2) which can be ope-

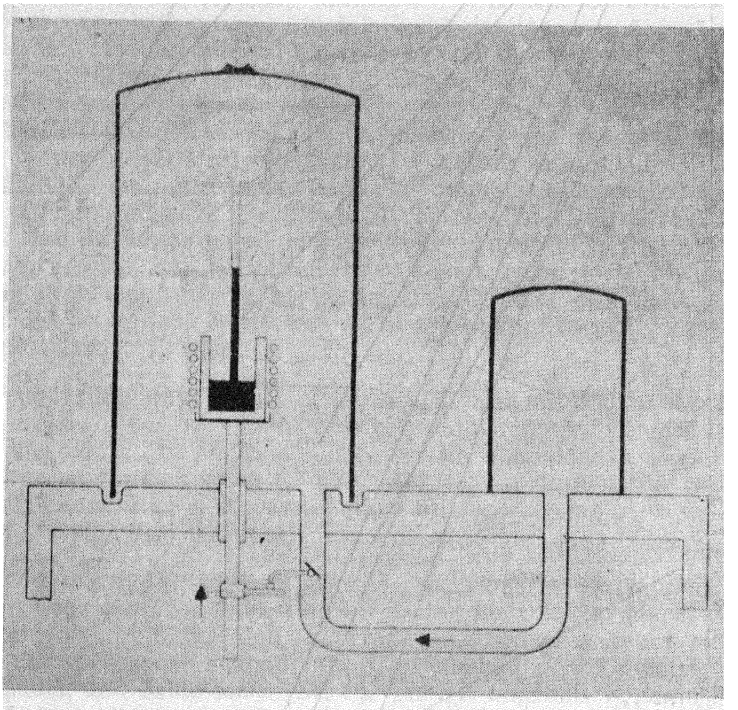

Fig. 2—Injection Casting Furnace

rated remotely may be successfully used to manufacture this fuel[14]. In practice, this would consist of a melting furnace connected to a supply of vacuum and high pressure argon. In the melting furnace there is a crucible with a molten charge of fuel. Above this is located a bundle of precision-bore, coated Vycor tubes which are closed at one end. After the furnace is evacuated it is disconnected from the vacuum system. Then the crucible containing the molten metal charge is raised to position which results in bringing the liquid level above the lower ends of the Vycor tubes. Simultaneously the furnace is pressured with argon. By the combination of pressure and inertia the metal fills the Vycor tubes. Later the Vycor tubes are broken away from the solidified uranium and the uranium pins are cut to desired length. Fuel of satisfactory appearance and good dimensional tole-

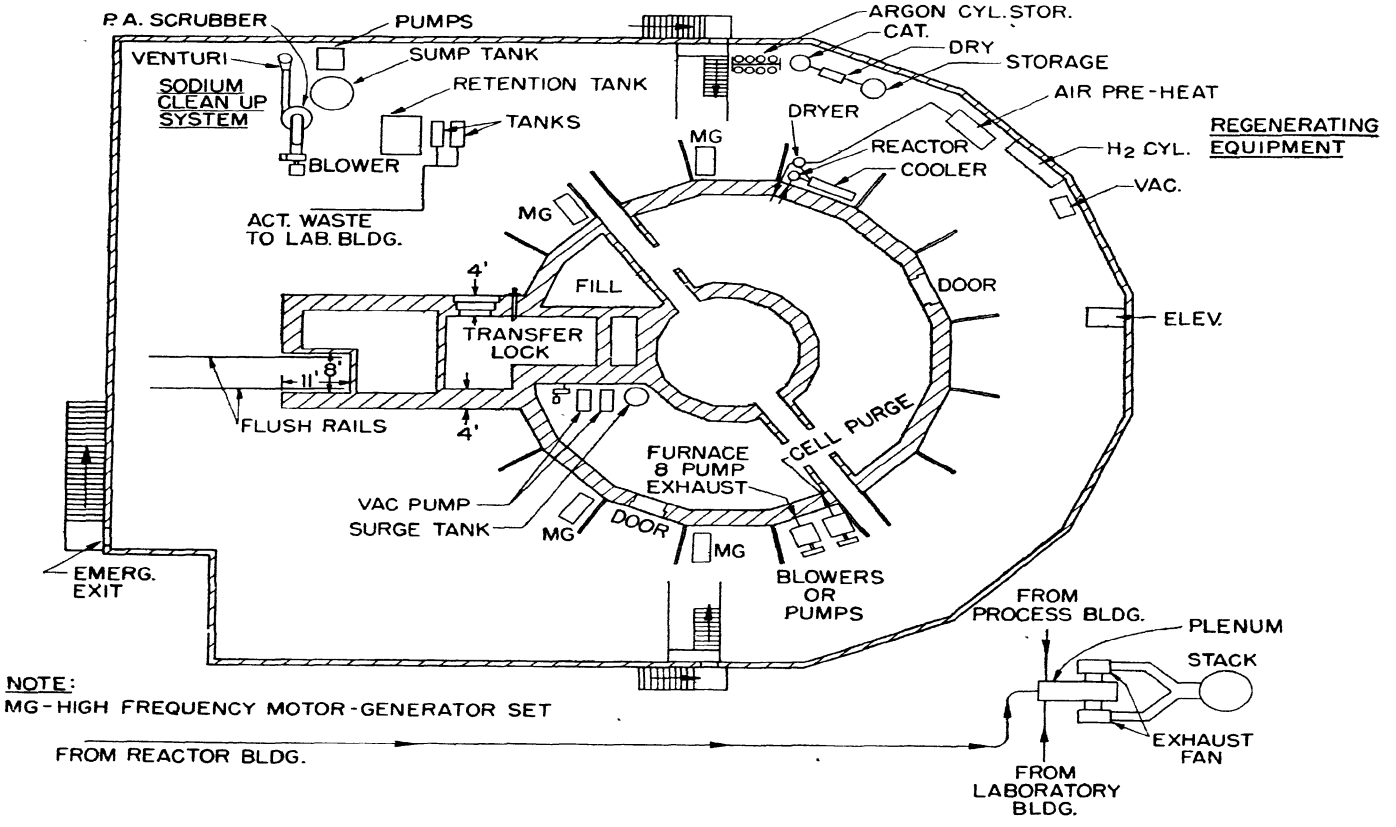

Fig. 3—Basement Plan EBR—II Process Building

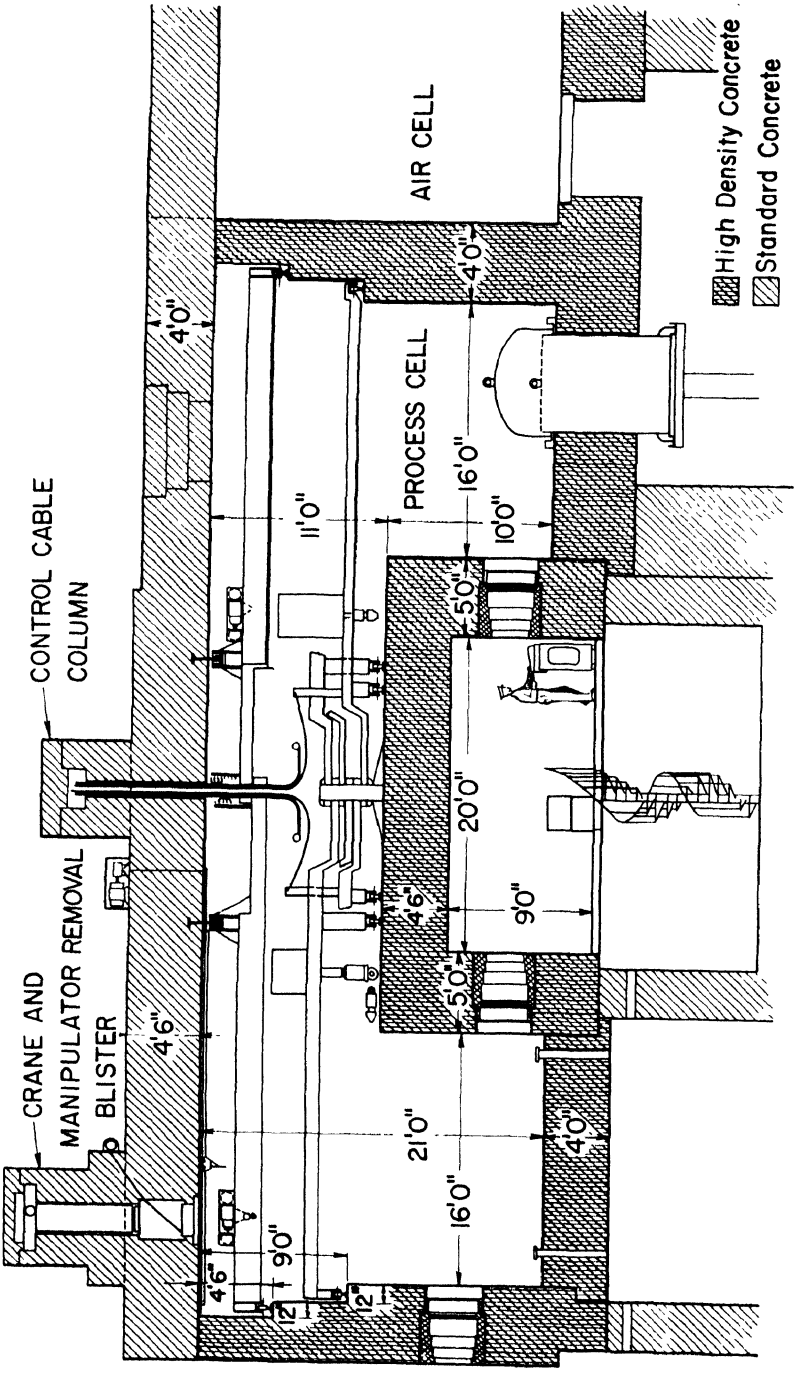

Fig. 4—Process Cell Design EBR—II

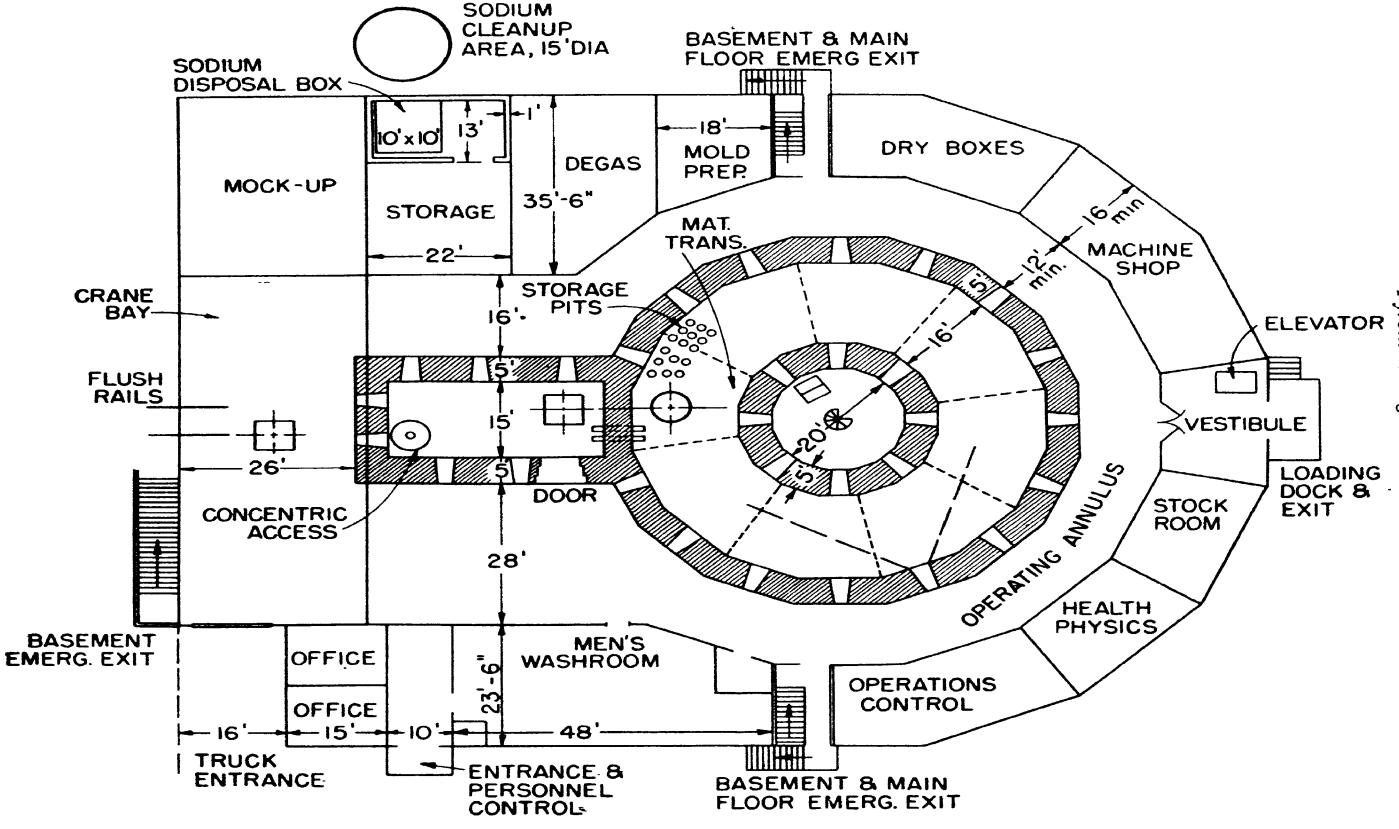

Fig. 5—Main Floor EBR—II Process Building

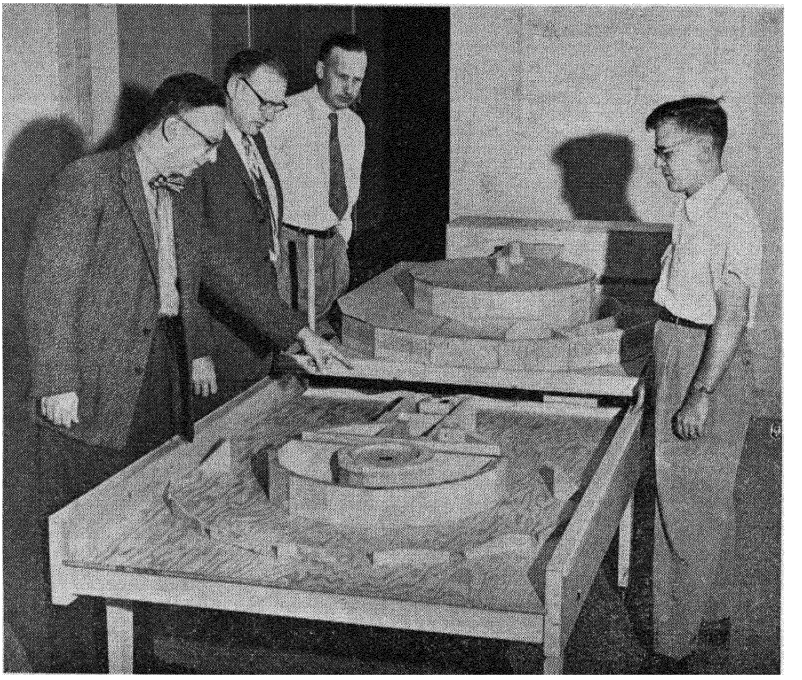

Fig. 6—EBR—II Process Building Model

rances has been produced in this manner. Procedures for remotely incorporating these pins into fuel assemblies are also being developed.

Proposed Application of Pyrometallurgical Processing

The first application of pyrometallurgical processing[1] will be made in connection with a 60 megawatt thermal experimental breeder reactor (EBR-II). Facilities are being designed (see Figures 3, 4, 5, 6 and 7) which will contain a pilot plant to handle all of the core processing by pyrometallurgical treatments. On a demonstration basis there will also be equipment for blanket processing.

The core treatment will consist of oxide drossing as the primary process and probably a zinc process for any supplementary processing. Since the required rate of core processing will be about five kilograms per day, detailed studies of process performance and equipment development are in progress for this scale of operation. Mock-up equipment has been built and its quantitative operation with a remotely-operated, heavy-duty manipulator is now in progress. (See Figures 8, 9, 10, and 11). Because of the high temperature of operation and the high level of radiation (fuel core expected to be processed after only 15 days' cooling), methods are being worked out for the purifica-

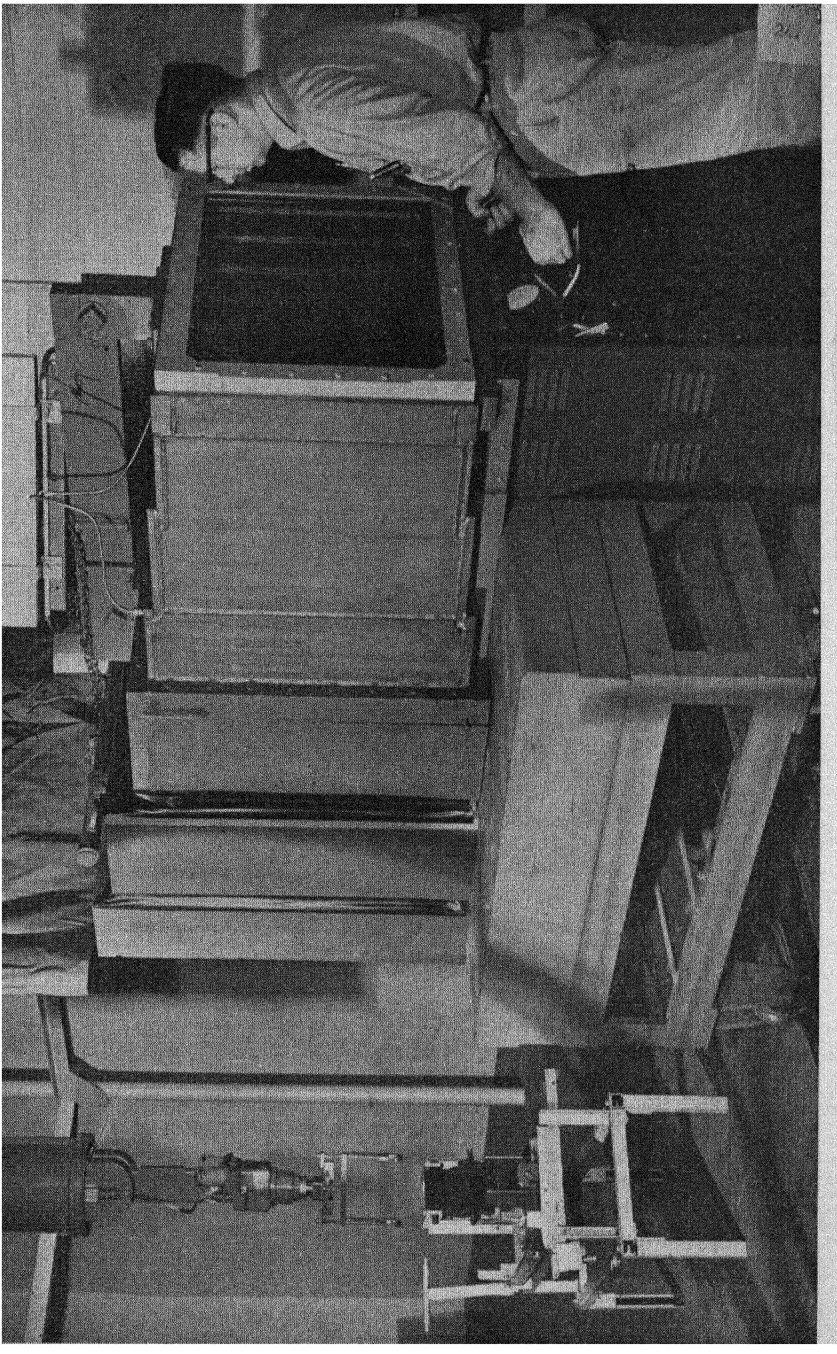

Fig. 7—EBR—II Mock-up. Operation of General Mills Manipulator through 5-foot Window

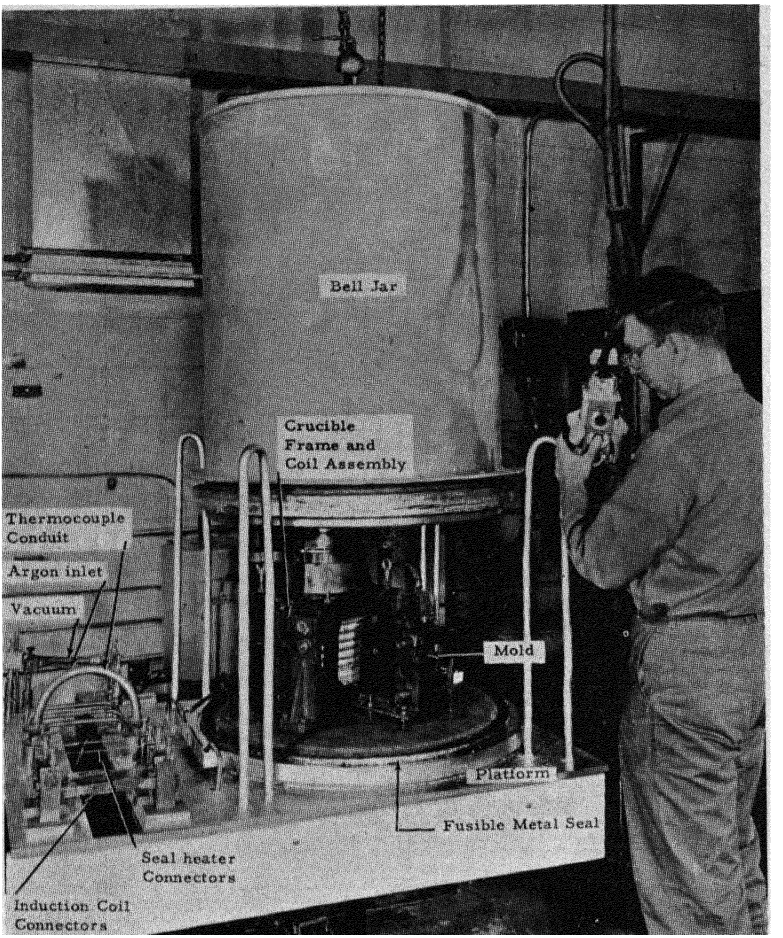

Fig. 8—Uranium Melting Furnace—Bell Jar Partially Removed.

tion and maintenance of satisfactory inert atmosphere for the process cell and for the development of components which will not suffer radiation damage. Procedures are also being worked out for handling and storage of the very active wastes which will be obtained at this plant. The scheduled completion date for this plant is near the end of 1959. Provisions for demonstrating blanket processing by molten magnesium extraction will be included in this plant. In addition, extra space is being provided to enable tests to be made of other promising pyrometallurgical methods which may be later developed for either core or blanket processing.

This plant will also be used to contain the equipment for remote fabrication of fuel. Altogether, this plant is being designed with the possi-

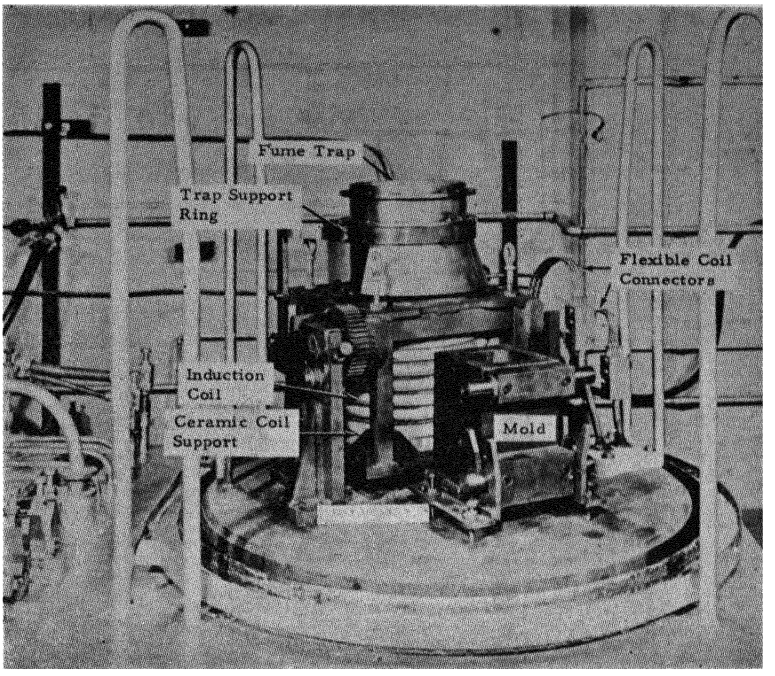

Fig. 9—Furnace Interior.

bility of handling plutonium-uranium fuels as well as enriched uranium fuels. Provisions for both of these fuels are desirable because the initial fuel will be enriched uranium but it is expected that later plutonium-uranium fuels will be used in this reactor.

The satisfactory development and operation of the integrated complex in this plant, namely, of reactor operation, fuel processing and fuel fabrication will be very significant because such an integration has heretofore not existed. Because of the experimental nature of the initial application of this concept, the plant is not expected to be economic, however, it is definitely expected that the results obtained from it can be used to assess the economic potential of this type of fuel and blanket processing as well as fuel re-fabrication. Savings are expected as the result of reduction in fuel inventory through immediate processing, use of simple and compact processes requiring little or no chemical conversion, recovery of expensive alloying agents, and simplification of waste disposal and criticality problems.

Acknowledgement

The work in the United States on pyrometallurgical treatment of reactor fuels and blanket has been done at Ames Laboratory, Argonne

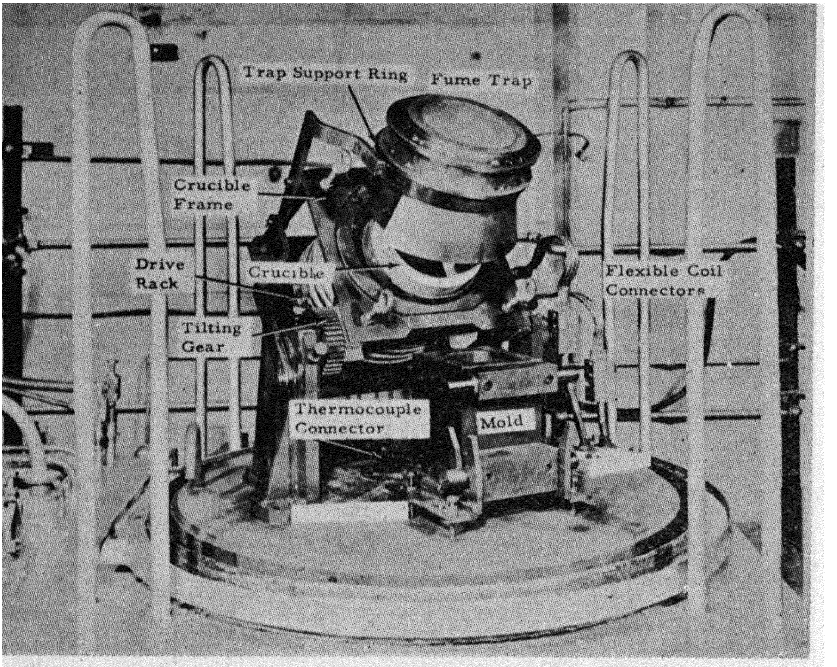

Fig. 10—Crucible Assembly in Partially Tilted Position

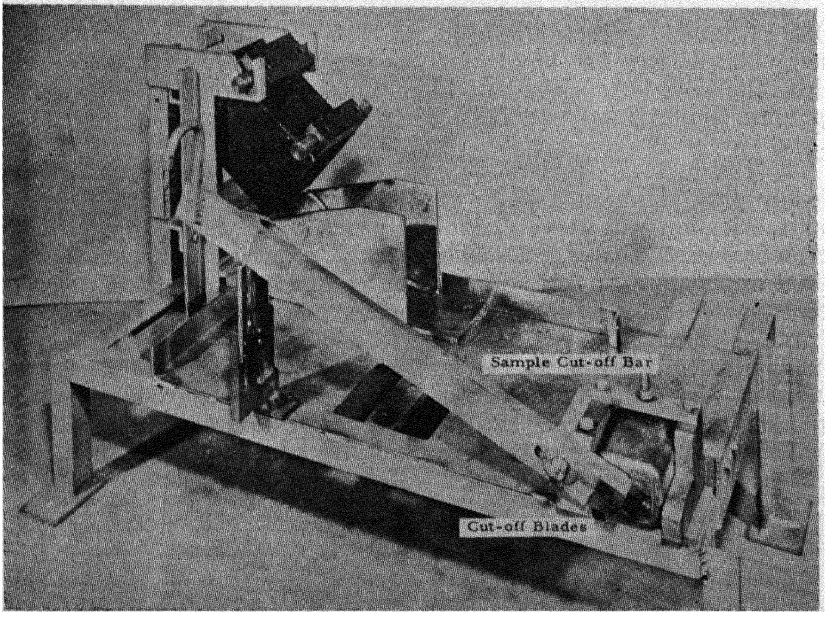

Fig. 11—Ingot Remover and Sampler.

National Laboratory, Atomics International, Brookhaven National Laboratory, Knolls Atomic Power Laboratory, Los Alamos Scientific Laboratory, and Oak Ridge National Laboratory. The contributions used herein are gratefully acknowledged.

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PHYSICAL METALLURGY OF URANIUM

By K. Tangri & R. Somasundaram *

Considerable information on uranium metallurgy has been accumulated in the laboratories of various countries in the last decade and a half. But, a sizable part of it still lies hidden under the dark shadow of the word "classified". This paper is aimed at presenting in brief the current status of our knowledge, as gathered from the open literature, regarding the properties and behaviour of metallic uranium and its alloys. An excellent review on this subject was presented in 1955 at the Geneva Conference by Frank G. Foote (1). While bringing the subject matter upto date, an attempt has also been made, by changing the emphasis on various topics covered, to make this work complementary rather than a duplication of the previous publication.

Physical Properties of Uranium

Certain of the physical properties such as density, specific and latent heats, vapour pressure, thermal conductivity and phase change temperatures are relatively independent of the prior metallurgical history or, within limits, the exact state of purity of the sample. Most of these selected data on these so called structure insensitive properties are listed in Table I, and the remaining summarized in Fig. 1 and 2.

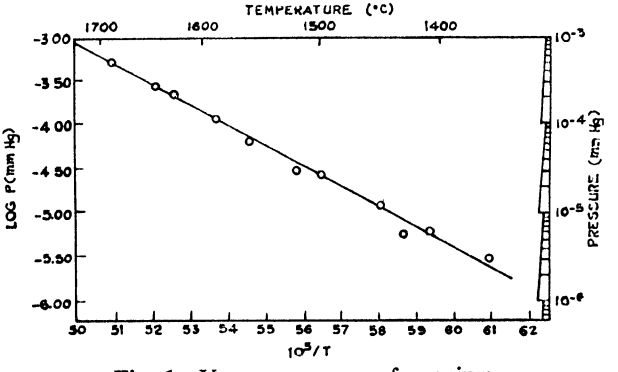

Fig. 1—Vapour pressure of uranium.

$$\log P \text{ (in mm)} = \frac{2330}{T} + 8.583.$$

Phase	Temp. (°C.)	No. of atoms per unit cell	Vol per atom (10^{-24} cm^3)	Density (gm/cc)
α	Room (25°C)	4	20.75	19.04
α	200	4	20.93	18.88
α	400	4	21.17	18.67
α	650	4	21.57	18.33
β	720	30	21.82	18.11
γ	805	2	21.88	18.06

* Metallurgy Division, Atomic Energy Establishment, Trombay, Bombay.

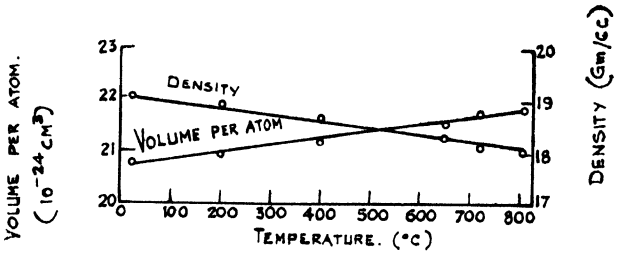

Fig. 2—Some physical constants of Uranium metal.

Table I.—Physical and thermal properties of uranium

Density :		
High purity uranium, directionally solidified (at 25°C)	19.05 ± 0.02 grams/cm³	(a)
Calculated from X-ray data on high purity uranium (at 25°C)	19.04 grams/cm³	(b)
Wrought material	18.7 to 19.08 grams/cm³	(c)
Transformation Points :		
α to β :	668°C	
β to γ	774°C	(d)
Melting Point	1132 ± 1°C	(e)
Boiling Point :		
Extrapolated from vapour pressure measurements	3818°C	(f)
Vapour Pressure from 1630 to 1970°K (see also Fig. 1)		
$\log p \text{ (mm) of H} = \frac{2330 \pm 21}{T\ (°K)} + (8.583 \pm 0.011)$		(f)
Heat of Fusion (estimate) :	4.7 kcal/mole	(f)
Heat of Vapourization :	106.7 ± 0.1 kcal/mole	(f)
Heat of Sublimation at 0°K :	116.6 ± 0.1 kcal/mole	(f)
Enthalpy at 25°C :	1521.4 ± 1.6 cal/mole	(g)
Heat Capacity at 25°C:	6.612 ± 0.007 cal/deg-mole	(g)
Entropy at 25°C :	11.99 ± 0.02 cal/deg-mole	(g)
Heats of transformation :		
$\alpha \rightarrow \beta$, $\triangle H$ at 668°C	0.674 kcal/mole	(h)
$\beta \rightarrow \gamma$, $\triangle H$ at 774°C	1.131 kcal/mole	(h)
Entropy of transformation :		
$\alpha \rightarrow \beta$, $\triangle S$ at 668°C	0.717 cal/deg-mole	(h)
$\beta \rightarrow \gamma$, $\triangle S$ at 774°C	1.081 cal/deg-mole	(h)
Thermal conductivity (70°C)	0.071 cal/cm-sec-°C	(i)
Temperature coefficient (100 — 225°C)	$+1.5 \times 10^{-5}$	
Temperature coefficient (225 — 450°C)	$+0.4 \times 10^{-5}$	(j)

(i) Crystallographic and Thermal Expansion Data

Lattice Constants: 1. Alpha Phase, Orthorhombic		Space Group-Cmcm		4 atoms per unit cell (k)
Temperature (°C)	Lattice Constants (A)	Volume of Unit call (10^{-24}cm^3)	Volume per atom (10^{-24}cm^3)	Calculated Density (gram cm^{-3})
Room (25°C) (b)	$a_0 = 2.8541 \pm 0.0003$ $b_0 = 5.8692 \pm 0.0015$ $c_0 = 4.9563 \pm 0.0004$	83.02	20.75	19.04
200 (1)	$a_0 = 2.8675$ $b_0 = 5.8660$ $c_0 = 4.9775$	83.73	20.93	18.88
400 (1)	$a_0 = 2.886$ $b_0 = 5.861$ $c_0 = 5.005$	84.66	21.17	18.67
650 (1)	$a_0 = 2.920$ $b_0 = 5.834$ $c_0 = 5.064$	86.27	21.57	18.33

Thermal expansions (10^{-6} per °C) from X-ray data, parallel to:

	axis	25–125°C	25–325°C	25–650°C
(1)	a_0	21.7	26.5	36.7
	b_0	–1.5	–2.4	–9.3
	c_0	23.2	23.9	34.2

II. Beta Phase, Tetragonal

720 (n)	$a_0 = 10.759 \pm 0.001$ $c_0 = 5.656 \pm 0.001$	654.7	21.82	18.11

II.—a. Beta Phase (1.4|a|o cr)
Tucker's (m) sample contained 1.4 a|o Cr and the beta phase was retained to room temperature. Thewlis (n) has also reported lattice constant values for a similar alloy at 720° and 20°C.

720 (n)	$a_0 = 10.763 \pm 0.005$ $b_0 = 5.652 \pm 0.005$	654.7	21.82	18.11
20 (n)	$a_0 = 10.590 \pm 0.001$ $b_0 = 5.634 \pm 0.001$	631.8	21.06	18.77
20 (m)	$a_0 = 10.52$ $c_0 = 5.57$			

Linear coefficients of thermal expansion from 20—720°C.

(n)	along a_0	$= 23 \times 10^{-3}$ per °C
	along c_0	$= 4.6 \times 10^{-6}$ °C

III Gamma Phase, Body-centered cubic, 2 atoms per unit cell (0)

(p) 805	$a_0 = 3.525$	43.76	21.88	18.06
(q) 800	$a_0 = 3.49$			
25	$a_0 = 3,474$	41.93	20.96	18.85

Value at 25°C extrapolated from measurements on U—Mo in which gama phase can be retained by quenching.
Approximate linear expansion coefficient = 18 x 10^{-6} per °C.

(ii) **Magnetic Properties.** (r)

Susceptibility (e.m.u/g)	Temperature (°C)
1.720	14
1.891	660
2.017	Throughout beta-phase range
2.074	913

(iii) **Thermoelectric Force.** (s)

Temperature (°C)	Thermoelectric Force mV against platinum
50	0.52 — 0.58
100	1.15 — 1.27
250	3.75 — 4.10
500	10.21 — 11.18
600	13.37 — 14.72
700	16.81 — 18.57
800	20.59 — 22.51
900	24.75 — 26.58

(iv) **Thermal Conductivity.** (t)

Temperature (°C)	Thermal Conductivity (cal cm^{-1} sec^{-1} $°C^{-1}$)			
	Cast uranium	Cast uranium	U—½ a/o Chromium	U—12.4 a/o Mo.
0	0.062$_9$	—	—	—
100	0.066$_8$	0 0695	0.0646	—
200	0.070$_6$	0.0744	0.0693	0.055
300	0.074$_5$	0.0793	0.0740	—
400	0.078$_3$	0.0842	0.0786	0.061 (380°C)
500	0 082$_2$	0.0891	0.0833	0.068 (487°C)
600	0.086$_1$	0.0940	0.0856 (550°C)	—
650	0.088$_1$	—	—	—
680	0.088$_2$	—	—	—
700	0.089$_1$	—	—	—
720	0.089$_9$	—	—	—
740	0.090$_7$	—	—	—
760	0.091$_5$	—	—	—

(v) **Electrical Resistivity.** (t)

Values ranging from 25.0 to 41.0 microhm cm have been reported for the room temperature resistivity of uranium, depending on purity and condition of the material.

Temperature (°C)	Resistivity (microhm cm)	
	Sintered U (18.64 density)	Cast U
0	32.2	—
100	38.8	37.3
200	45.3	43.8
300	50.5	49.4
400	55.0	53.4
500	58.2	56.5
600	59.8	58.4
650	57.4	58.9
700	57.8	56.8
750	58.3	—
800	56.9	—
900	58.7	—

(a) B. Blumenthal, Argonne National Laboratory.
(b) M. H. Mueller, Argonne National Laboratory.
(c) J. H. Kittel, Argonne National Laboratory.
(d) Selected values from several sources.
(e) A. I. Dahl and H. E. Cleaves, **The Freezing Point of Uranium,** J. Research Natl. Bur. Standards 43:513 (1949).
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(i) J. L. Weeks, **Thermal Conductivity of Uranium and Several Uranium Alloys,** J. Metals 7, AIME Trans, 203:192 (1955).
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(m) C. W. Tucker, Acta Cryst. 4: 425 (1951); see also C. W. Tucker and P. Senio, **The Refined Crystal Structure of Beta Uranium,** KAPL—844 (1952).
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(o) Battelle Memorial Institute.
(p) J. Thewlis, **Structure of Uranium, Nature** 168:198, 1951.
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(s) A. C. Roberts and A. H. Cottrell, Phil. Mag, (8th series) 1 Ang. 1956, P. 711—717.
(t) I G. Culcheth, U. K. A.E.A.

Plastic Deformation Mechanism in Alpha Uranium

Crystallography of Twinning, slip and kinking: Studies of the crystallography of twinning, slip and kinking in alpha uranium have been carried out by R. W. Cahn[2] in Atomic Energy Research Establishment at Harwell. In default of single crystals, very coarse grained uranium was used for experiments. The various crystallographic elements of the four systems of twinning, two of slip and one of kinking as reported by Cahn are tabulated in Table II.

More recently, studies of the plastic deformation mechanisms in alpha uranium at room temperature have been carried out by L. T. Lloyd and H. H. Chiswik[3] at Argonne National Laboratory (ANL). The operative deformation elements in alpha uranium have been determined as a function of the crystallographic direction of testing. Single crystals, produced by grain coarsening techniques, were tested under compression at room temperature. The findings of these investigators, which confirm Cahn's data only partially, are set down in Table III.

The deformation mechanisms noted may be arranged with respect to their frequency of occurrance and ease of operation in the following order :

1—(010)—[100] Slip, 2—$\{130\}$ twinning, 3—$\{\sim 172\}$ twinning, and 4—under special conditions of stress application, kinking cross—slip, $\{176\}$ twinning, and $\{011\}$ slip. The composition planes of the $\{172\}$ and $\{176\}$ systems were found to be irrational. Cross—slip was shown to be associated with the major (010) slip system, coupled with localised interaction of slip on the (001) planes. In a cross-slip system the slip direction should be common to both cooperating planes, which in this case would be the [100] direction. The mechanism of kinking was found to be similar to that observed in other metals in that it occurred chiefly when the compression direction was nearly parallel to the principal slip direction [100] and was associated with a lattice rotation about an axis contained in the slip plane and normal to the slip direction: the [001] in the uranium lattice. The resolved critical shear stress for slip on the (010)—[100] system was found to be 0.34 kg. per mm^2.

Effect of Temperature on Twinning and Slip : Systematic studies of the influence of temperature on twinning and slip in uranium have not been reported. From the incidental observations made during his experiments with coarse grained uranium, Cahn found that the specimens deformed at 300°C twinned profusely. A specimen deformed slowly at 450°C was found to be almost devoid of twins, whereas specimens deformed at 550°C and 630°C were entirely devoid of twinning. From these observations it was concluded that somewhere between 300°C and 450°C, twinning is almost entirely superseded by slip. But, in a test on a single crystal of uranium, Lloyd and Chiswik

Table II.—Crystallographic elements for twinning, slip and kinking in uranium according to Cahn

Twinning	K_1	K_2	n_1	n_2	2ϕ	S
	(130)	(110)	[310]	[110]	81° 30′	0.299
	∽ (172)	(1$\bar{1}$2)	[312]	∽[372]	83° 30′	0.228
	(112)	∽ (172)	∽ [372]	[312]	83° 30′	0.228
	(121)	∽ (14$\bar{1}$)	∽ [321]	[311]	80° 40′	0.329
Slip	K					
	(010)	[100]				
	(110)	[110]				
Kinking	K					
	(100)	[001]				

Table III—Crystallographic elements for twinning, slip and kinking in uranium according to Lloyd and Chiswik

Twining	K_1	K_2	n_1	n_2	2 O	S
	(130)	(110)	[3$\bar{1}$0]	[110]	81° 30′	0.299
	∽ (172)	(112)	[312]	∽	83° 32′	0 229
	∽ (176)	(111)	[512]	∽	83° 50′	0.216
Slip	K					
	(010)	[100]				
	(010) (001)	[100]				
	(011)	[100]				
Kinking	K					
	(100)	[001]				

N.B. The sign ∽ denotes the absence of rational indices. The value which follows is therefore approximate.

have shown that under compression in suitable direction twinning on the {130} also occurs at 600°C. This disparity in the two findings is very probably due to the differences in the grain size of the specimens, and the rate of deformation, and also the presence of grain boundaries in Cahn's specimens, which are known to affect twinning in metals.

Incidental observations on the effect of temperature on slip in uranium have also been made by Cahn. He found that raising the temperature of deformation causes the (010) slip lines to become somewhat more widely spaced and thicker, and the amount of cross-slip to increase so much that the slip lines become wavy.

Preferred Orientation in Alpha Uranium

As plastic deformation occurs more easily along certain directions of the individual crystals within a polycrystalline aggregate, it causes

certain favoured orientations of crystallographic planes and directions, which depend on the particular type of deformation imposed and the temperature at which it is carried out. It is then said that the aggregate has assumed a deformation texture or acquired a preferred orientation. Because of the anisotropic nature of alpha uranium, some of its important physical and mechanical properties, as we will discuss later, are greatly affected by the presence or absence of a preferred orientation.

Most of the recent investigations of the preferred orientation in uranium have been carried out by Geiger—Counter X—ray Diffractometer techniques, which yield more precise quantitative data than the older and time consuming X—ray photographic methods. Several different types of specimen holders have been designed and built, based on the basic techniques developed by L. G. Schulz[4], L. K. Jetter, B. S. Borie, Jr.[5] and G. B. Harris[6] for imparting the necessary motions or rotations to the specimen in order to collect the necessary intensity data from the X—ray diffraction for the construction of pole figures, pole charts and inverse pole figures.

As Fabricated (Rolled, Swaged or Extrued) and Recrystallized Rod : The type of preferred orientation and its intensity depends also on the amount of cross-sectional reduction given, the temperature of working and in general, on the metallurgial history of the starting material.

Textures developed in rods randomized by beta treatment (one minute in lead at 720°C and water quenched) and subsequently rolled at 300°C (93% total reduction) and 600°C (83% total reduction) have been examined by W. P. Chernock and P. A. Beck[7]. The rolling textures were found to consist of two fiber texture components, in which the (010) and the (110) planes are perpendicular to the rod axis. A schematic representation of the duplex fiber texture described above is shown in fig. 3. The relative amounts of these two components vary, depending upon temperature of rolling. The (010) component seems to predominate at the lower temperature and (110) at the higher temperature.

Recently a systematic study of the textures developed in a number of uranium rods rolled (75% total reduction) at 300°, 400°, 500°, 600° and 640°C has been made by M. H. Mueller and H. W. Knott[8]. The pole charts obtained from these rods indicate that the rods rolled at the lower temperatures show approximate (010) and (120) components with the (010) predominating. There is a gradual decrease of the (010) component with the increasing rolling temperature and a corresponding increase of the (120) component. At the higher temperatures the (120) component shifts to an approximate (110) with a minor (010) component.

M. H. Mueller, H. W. Knott and P. A. Beck[9] have reported that if uranium rods are rolled at 300°C to a sufficiently high reduction

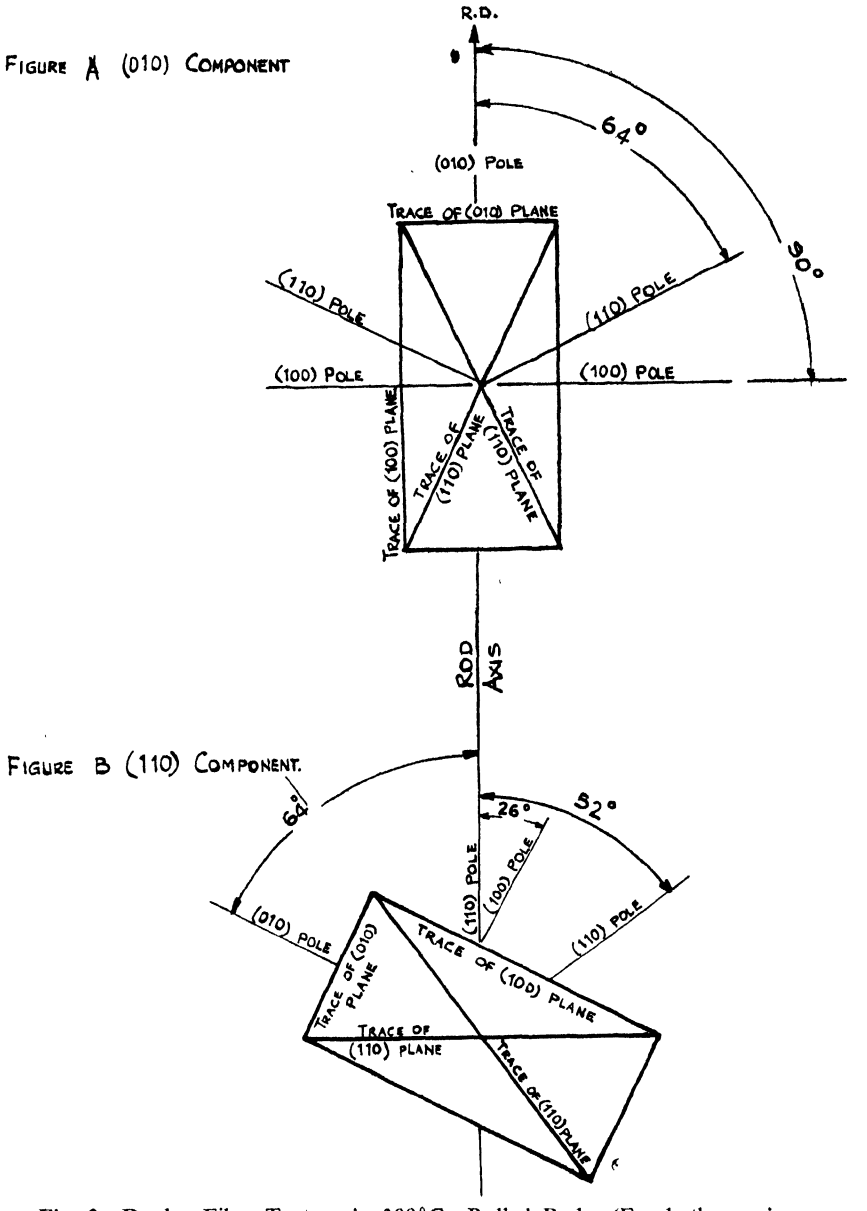

Fig. 3—Duplex Fiber Texture in 300°C—Rolled Rod. (For both uranium crystals shown the (001) plane is the plane of the drawing.

(70% or greater) the texture produced is practically the same regardless of the previous history. The texture obtained after 70% reduction may be described by a concentration of the fiber axis between

(010) and (041) with considerable scatter in the direction of (100) including a minor maximum near (120). Below 70% reduction the type of orientation obtained may vary considerably, depending upon the starting material. For example, the inverse pole figures shown in fig. 4 indicate that the beta treated material which was mainly random, shows a gradual increase of fiber axis concentration near the (010) and (120) poles as the amount of reduction at 300°C is increased

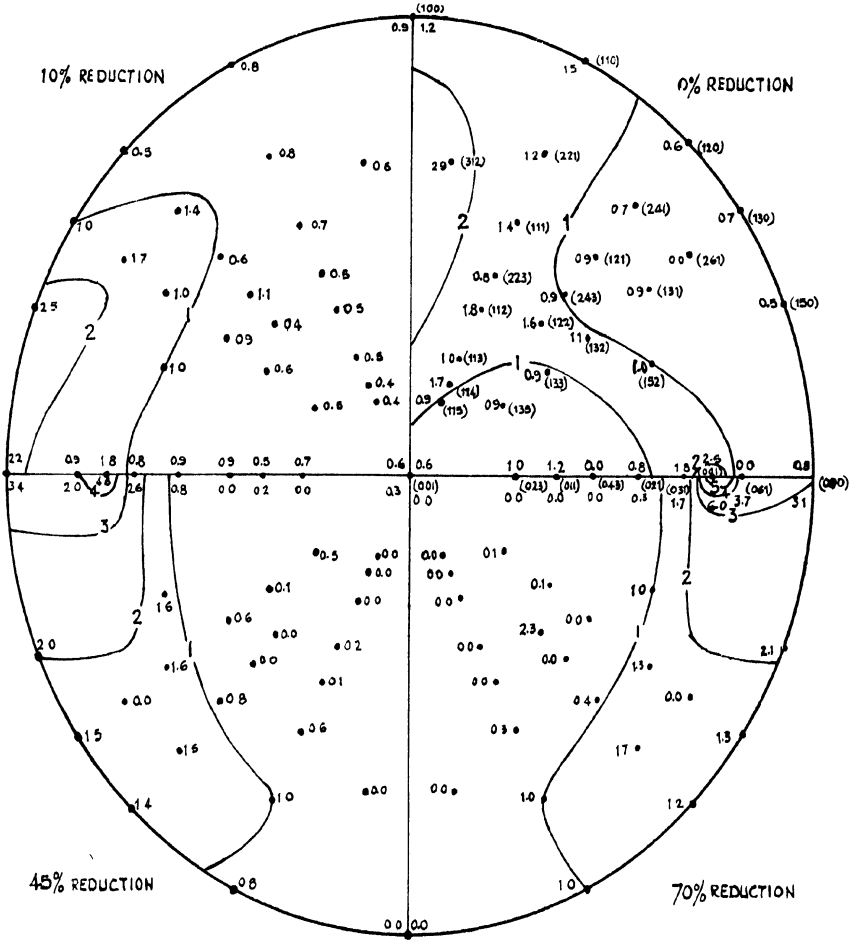

Fig. 4—Inverse pole figure of uranium rods rolled at 300°C. (0,10,45 and 70% reductions) Initial condition-water quenched from the beta phase.

Since considerable spread in intensity has been observed, some workers have indicated that some of this intensity might be accounted for by minor texture components such as (451), (021), (131) in rolled rods or [031], [431], [100] directions found in 500°C swaged rods.

L. K. Jetter [10] has reported the texture of a 500°C swaged rod (see fig. 5) as a duplex texture with the [010] direction and the [410[direction parallel to the rolling direction. The [410] direction is nearly parallel to the (110) pole, as may be seen in fig. 6, so that,

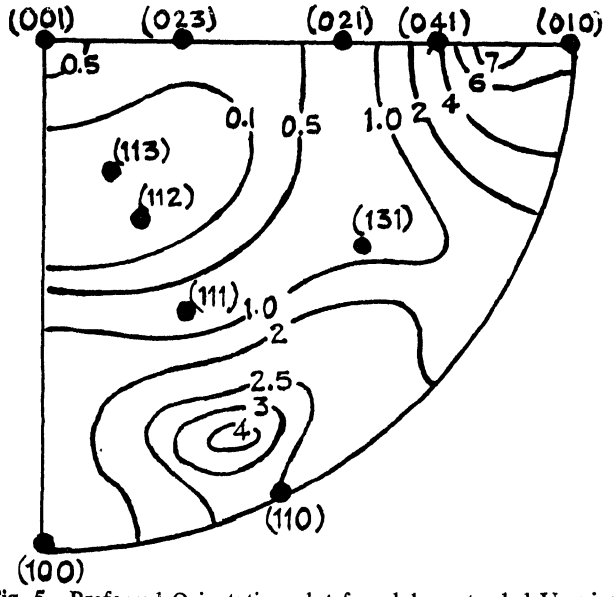

Fig. 5—Preferred Orientation plot for alpha extruded Uranium Rod, as extruded.

this texture is practically identical with the duplex rolling texture reported by various investigators.

A study of the effect of rollpass design on the radial symmetry of the texture produced has been made by M. H. Mueller and H. W. Knott[8]. A plot of the radial distribution of the (002) poles indicates an asymmetric pattern with the oval, edge-oval pass sequence and a rather uniform distribution of these poles with the hand round roll passes (figs. 7 and 8).

As a result of earlier work done by X-ray photographic techniques, it was felt that the texture of swaged or rolled uranium rods did not change after recrystallization. However, recent work[7] by using a more precise X-ray diffractometer technique, has indicated that in rods rolled at lower temperatures, (i.e., rods having mainly the (010) rolling texture) the (010) component remained after recrystallization though it may be decreased in amount, and that the (110) componen is replaced by an approximately (140) component with considerable spread which in some cases has been described as a (131) orientation A schematic representation of the recrystallization texture of a 300°C —rolled and 575°C—recrystallized rod is shown in fig. 9. But rod

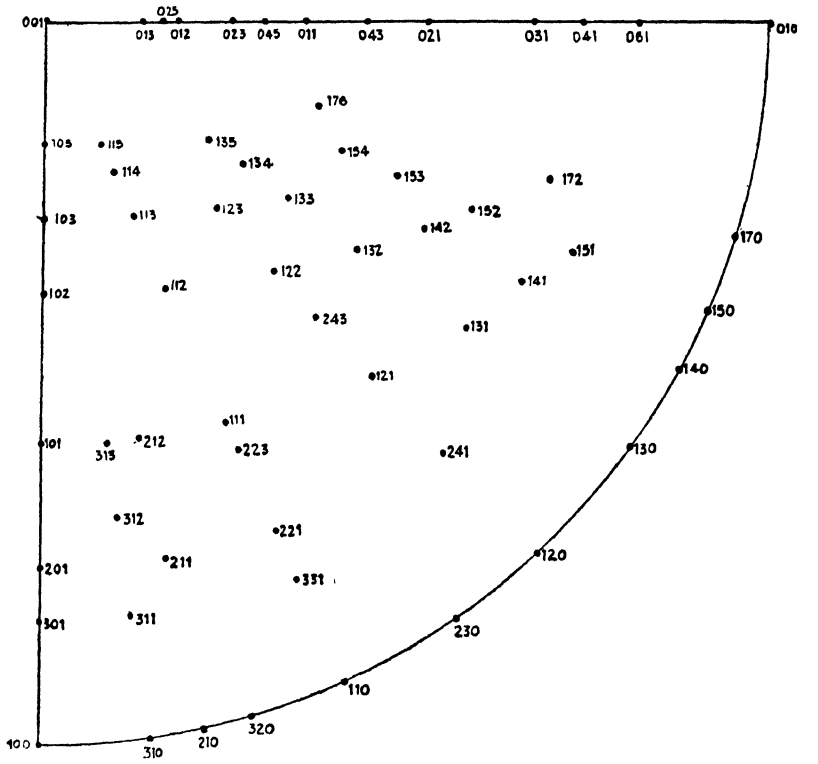

Fig. 6a—(001) standard projection of alpha-uranium plane poles.

rolled at higher temperature (around 600°C) have been found to show very little textural change on annealing in the high alpha range[8].

The fact, that uranium rods which are either slow or fast beta treated after deformation assume a very nearly random orientation, has been amply confirmed by various investigators in many laboratories.

Powder Compacts : X-ray diffractometer investigations of the preferred orientation in hot pressed uranium compacts carried out by M. H. Mueller[1] M. J. Sanderson[1], and K. Tangri and H. Q. Fuller[1] indicated that there appeared to be very little orientation and the samples were essentially random.

As Rolled and Annealed Sheet and Strip : The textures produced in uranium sheet rolled under various condition of temperature and amount of reduction have been reported by Seymour[12], Mitchell and Rowland [13], Adam and Stephenson[14] and Mueller and Knott and Beck[15].

The differences in the metallurgical histories of the specimens used

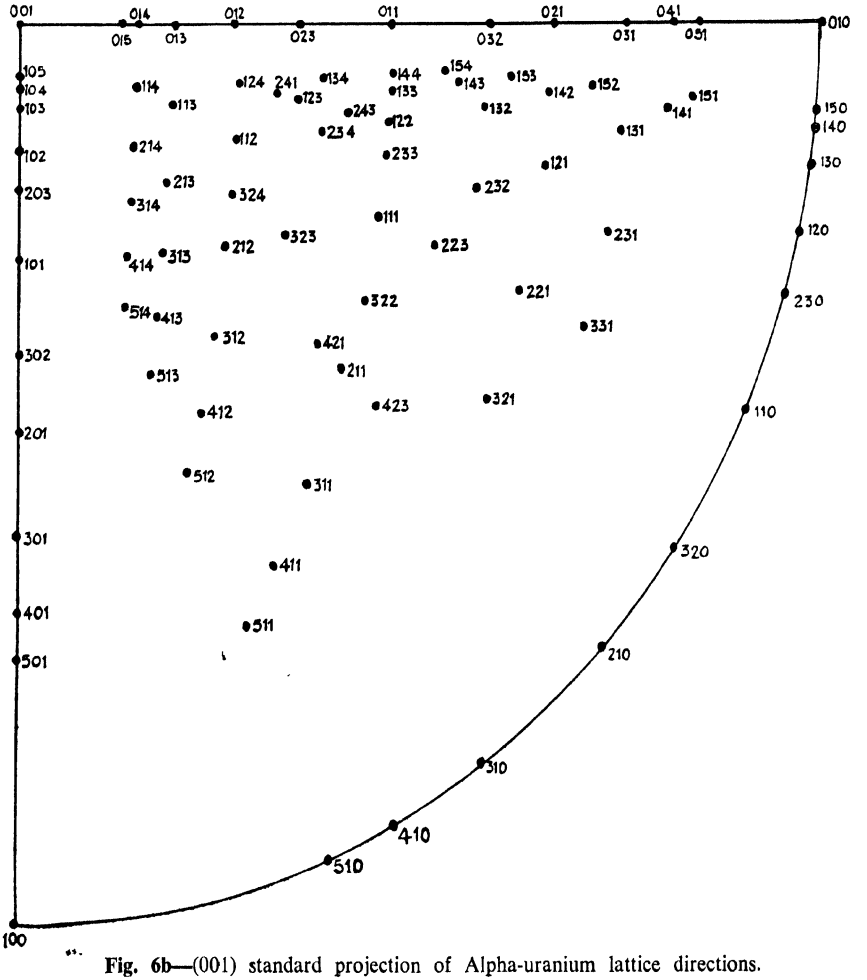

Fig. 6b—(001) standard projection of Alpha-uranium lattice directions.

by these workers are largely responsible for the differences in their pole figures. However, it was observed in general that there was a high (010) pole concentration in "as rolled" material near the rolling direction as shown in Fig. 10. In sheet rolled at the higher temperatures there was also a high (110) pole concentration near the rolling direction. In addition, the (001) pole figures showed a high concentration near the center of the pole figures but displaced towards the transverse direction and in some cases towards the rolling direction.

The pole figures for the 300°C rolled uranium sheet after recrystallization at 525°C are shown in Fig. 11. The (010) pole figure is very similar to that obtained for the as rolled sheet; however, the distribution of the (110) and (100) pole intensity has changed considerably.

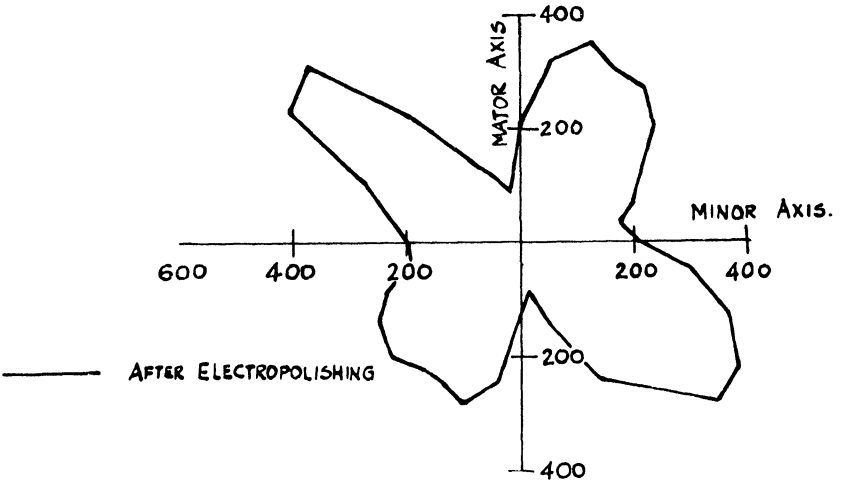

Fig. 7—Radial intensity of the (002) reflection from a 1″ round uranium rod rolled in an oval, edge-oval pass sequence (Cu K radiation, using 0.2° geiger tube slit and 1° x-ray tube slit.)

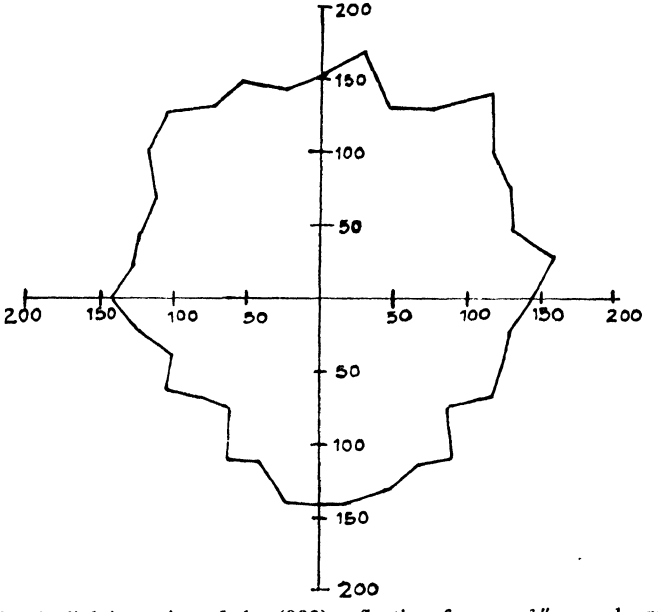

Fig. 8—Radial intensity of the (002) reflection form a ¾″ round uranium rod rolled with hand round pass rolls. (Cu K ∝ radiation, using 0.2° geiger tube slit and 0.4° x-ray tube slit.)

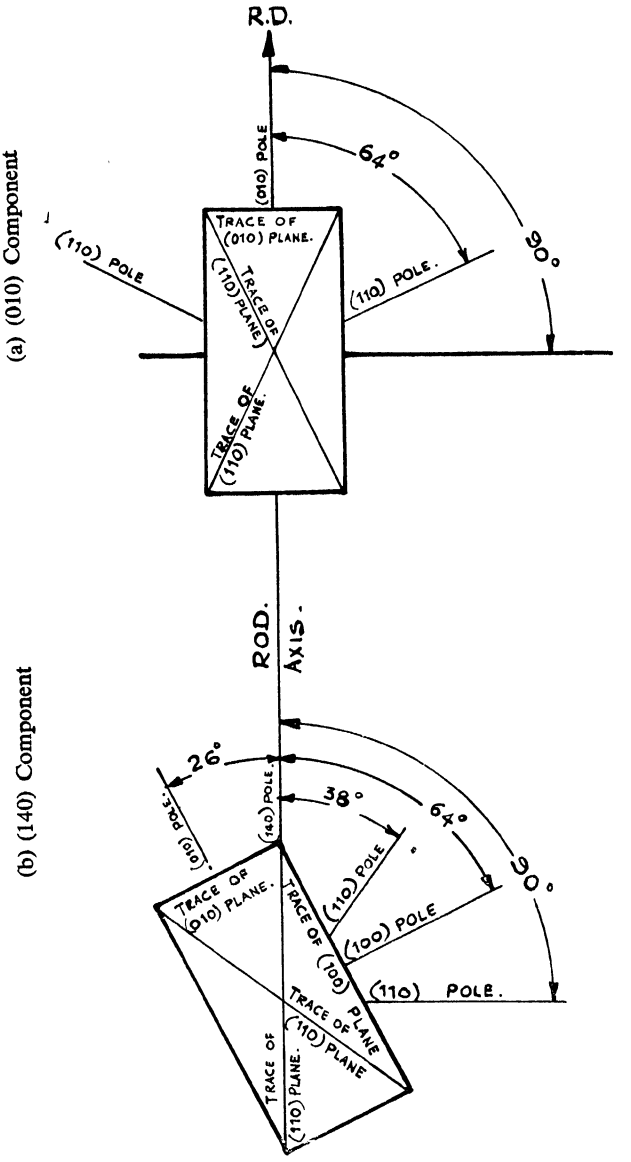

Fig. 9—Duplex fibre textile in 300°C-rolled, 575°C—recrystallized rod. (For both crystals the (001) plane is the plane of drawing.)

Fabrication of Uranium

Due to the three allottropic modifications in uranium, the working chracteristics of this metal are largely dependent upon the temperature

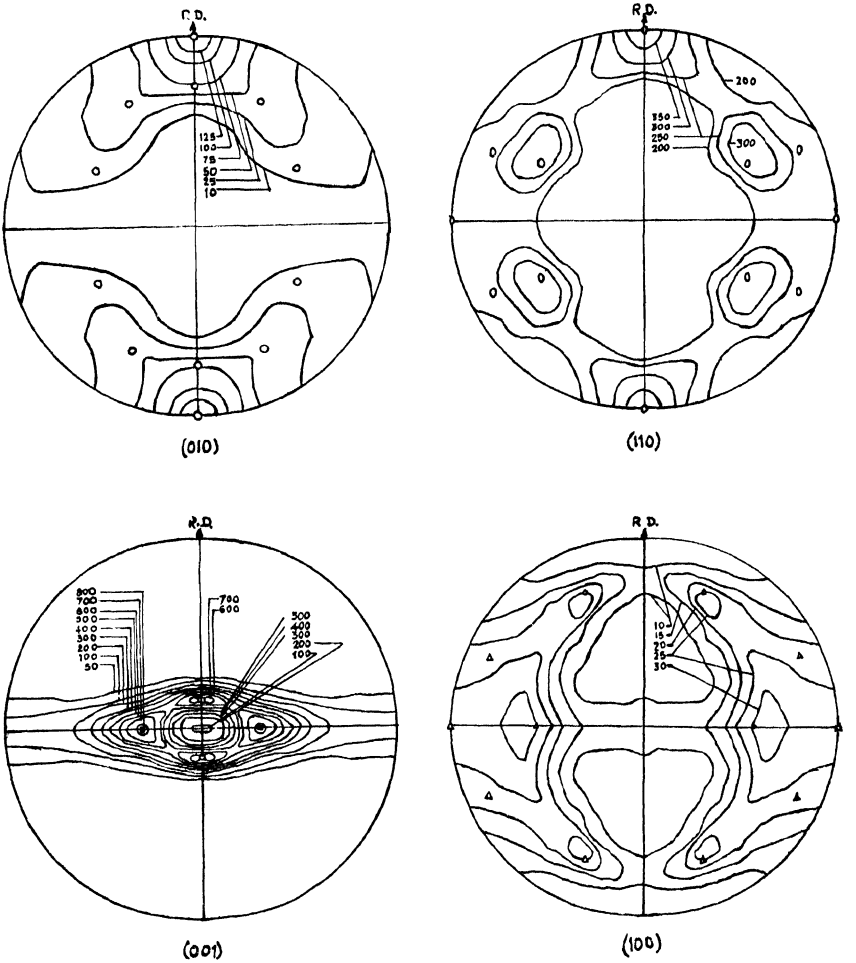

Fig. 10—Pole figures for uranium sheet rolled at 300°C to an 87% reduction.

of working. At lower temperatures (upto 450°C) deformation takes place by twinning and work hardening occurs, but at higher temperatures, the twinning mechanism is replaced by a slip mechanism and at the same time annealing and recrystallization during working becomes possible. The variation in hardness of uranium with temperature is shown in Fig. 12.

Fabrication methods commonly employed for other engineering materials are also applicable to uranium but the only ones so far used to any practical extent are rolling and extrusion. Rolling temperatures within the range 400°C-600°C are employed to take advantage of the decrease in hardness and increase in ductility with increase of temperature within the alpha range. Temperatures within the range of

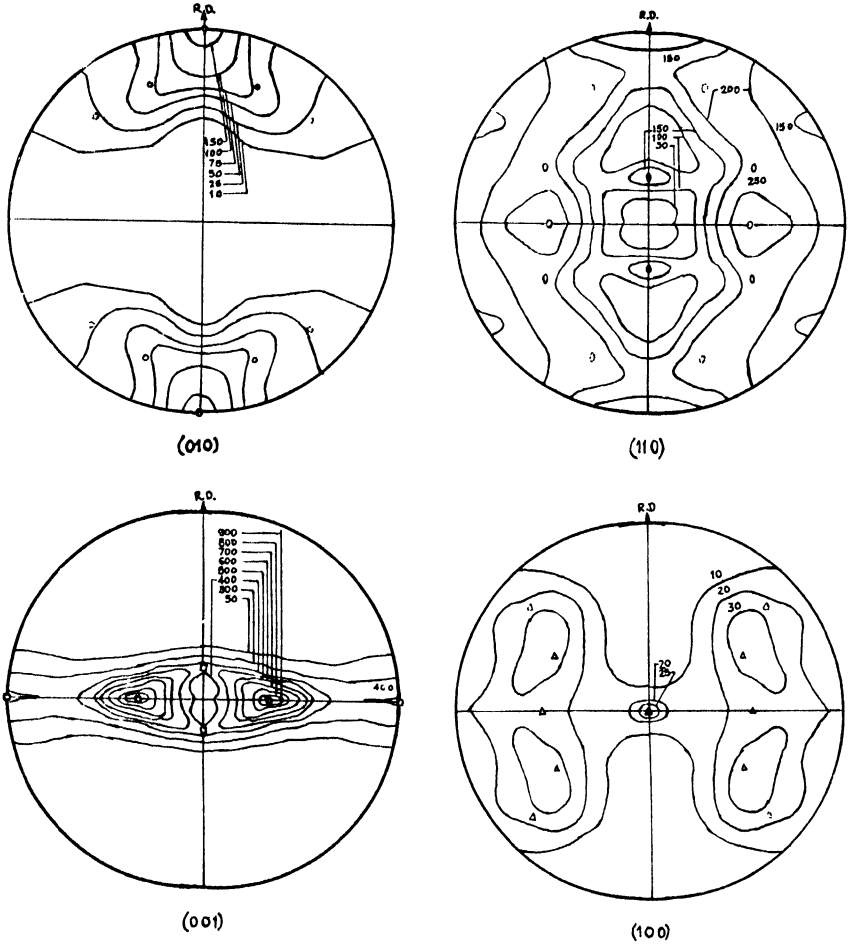

Fig. 11—Pole figures for Uranium Sheet 300°C rolled and recrystallized.

660-770°C are not very practicable because the forces required to hot work the relatively hard and brittle beta phase are from 2 to 3 times as great as at 650°C (16). Above 770°C uranium rolls easily, but the material is so soft that bars in this temperature range are very difficult to handle, owing to their high density and very low resistance to deformation.

Conventional steel type rolling mills are satisfactory for producing uranium bar. However, round passes are preferred to oval and gothic passes for the following reasons. Firstly, the roll contact with the greater part of the surface of the bar results in the compaction of oxide skin, thereby reducing the amount of oxidation; secondly, in a round pass, the majority of the uranium bar is under compression, and therefore, less likely to crack than when an appreciable amount is free from

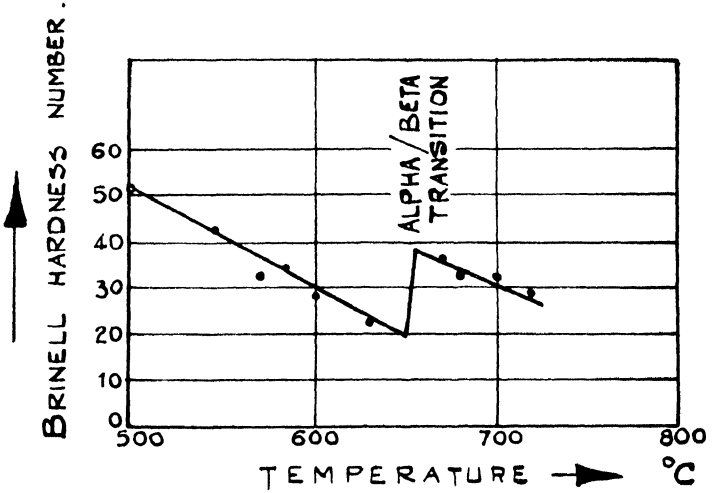

Fig. 12—The variation in hardness of Uranium with temperature. (Munro.)

the rolls, and therefore under tension only. Furthermore, it has already been mentioned that the radial distribution of the (002) planes which lie parallel to the rod axis, is nearly symmetrical in a rod rolled with hand round passes, as contrasted to the highly asymmetrical pattern that results from the oval, edge-oval pass sequence. It is quite likely that the asymmetric nature of the probable residual texture after beta treatment would adversely affect the mechanical stability of the uranium bar under actual working conditions.

In sheet or strip rolling, due to the larger ratio of area to volume and the attendant danger of greater oxidation, enclosing the uranium in a less readily oxidizable metal, such as nickel, becomes necessary. A graphite or other barrier film must be provided between uranium and nickel to prevent alloying. After rolling to about 0.05 in. the uranium can be removed from its protective sheath and finished by pack or cold rolling. Uranium foil of 0.0005 in. thickness has been produced by such a process.

Extrusion is usually carried out at temperature above 770°C because of the lower loads required to deform the gamma phase; bending of the product can be avoided by extruding vertically downward. Because uranium alloys rapidly with metals of the iron, nickel and cobalt group (usual constituents of die materials) at 735°C, precautions have to be taken to avoid contact. A thick graphite separating layer has been used in France but the most satisfactory material so far used has been stellite. Successful extrusion has also been carried out in bonded titanium carbide or tungsten carbide dies. The main disadvantage, however, of these high temperature die material is their brittleness. Because of these difficulties some extrusion has been done at temperature of 500°C-600°C.

Uranium can also be fabricated by powder metallurgy techniques, although it sinters only at temperatures above 80% of the melting point in contrast with nickel and other metals which densify at 50% of their melting temperatures. In compacts of minus 300 mesh powder, cold pressed at 70 ton/in^2 and sintered in vacuum at 1125°C, 94% of the theoretical densities have been achieved. Material of slightly higher density and with a considerably finer and randomly oriented grain structure can be produced by hot pressing (around 600°C) in vacuum at about 20 tons/in^2 (17).

The problem of machining uranium is dominated by two basic problems; the metal work hardens rapidly and it readily oxidizes. Therefore, machining technique demands fast and deep (a minimum of 0.025 in.) cuts so that the surface metal can be removed before it is hardened. Carbide tipped tools with mineral oil or water-soluble oil coolants have been found satisfactory (18).

The extreme reactivity of uranium at high temperatures poses a serious problem during brazing and welding. Some measure of success has been achieved with argon pressure-welding using high frequency heating. Welds made under pressure of 5-10 ton/in.^{2} at temperatures in alpha phase have been reported to have tensile strengths about 80% of that of the parent metal (17).

Heat Treatment of Uranium

A desirable metallurgical structure of fabricated uranium for use in a reactor may be described as consisting of randomly oriented and equiaxed fine grains with a minimum of variation in the average grain size. Keeping these basic requirements in mind, the effect of some of the more important variables that affect recrystallization and grain growth in uranium are summarized.

Due to the large number and complexity of the variables involved in the recrystallization behaviour of uranium, and also because of the urgent need of practical information in the last few years, systematic data of a quantitatively reliable nature is rather scarce. However, data on the recrystallization temperature and time of uranium with a variety of metallurgical histories are presented in summary form in Tables IV and V and Fig. 13.

An evaluation of the various techniques employed for attempting the production of single crystals of uranium is also presented in brief.

Uniformity of Recrystallized Structure : The anistropic properties of alpha and beta uranium result in non-uniform microstructure on annealing. Rods or plates rolled to high reductions at 600°C show banding on annealing. The average size and the orientation of recrystallized grains in different bands vary considerably. It seems that the bands are formed due to the differences in degree and modes of de-

Table IV—Reconstallization data on Uranium

Worker	Metallurgical History of Specimen	Annealing Time	Recrystallization Temperature	Remarks
E. S. Fisher (1)	A. Impure material plus tantalum.	One hour	475°C	Completely recrystallized.
	B. High purity uranium, with low concentration of submicroscopic inclusions. Both rods A and B reduced by a step reduction process with a 50% final reduction at 300°C.	One hour	425°C	Completely recrystallized.
E. E. Hayes (18A)	A. 500 ppm. C, 60 ppm. Fe, sheet specimens rolled at room temperature, reductions 2 to 94%.	1¼ hours	See fig. 13	
	B. Same material as A, but only 85% reduction at room temperature.	See table V.	350° to 500°C	
K. M. Mayfield (1)	Rods rolled on a single stand mill, finishing temperatures less than 600°C			Not completely recrystallized during rolling.
S. P. Rideout (1)	Rods rolled in a 6-stand commercial mill, finishing temperature :			
	A. 480°C	Over 20 minutes	500°C	Completely recrystallized
	B. 500°C			Completely recrystallized during rolling.

Table V—Effect of time on recrystallization range after 85% reduction at room temperature of impure material (E. E. Hayes, MIT)

Annealing Temperature (°C)	Recrystallization Time	
	Beginning	Complete
350	Over 2 weeks	
375	Over 1 week	
400	24 hours	
425	1¼ hours	24 hours
450	5 minutes	1¼ hours
475	1 minute	5 minutes
500		1 minute

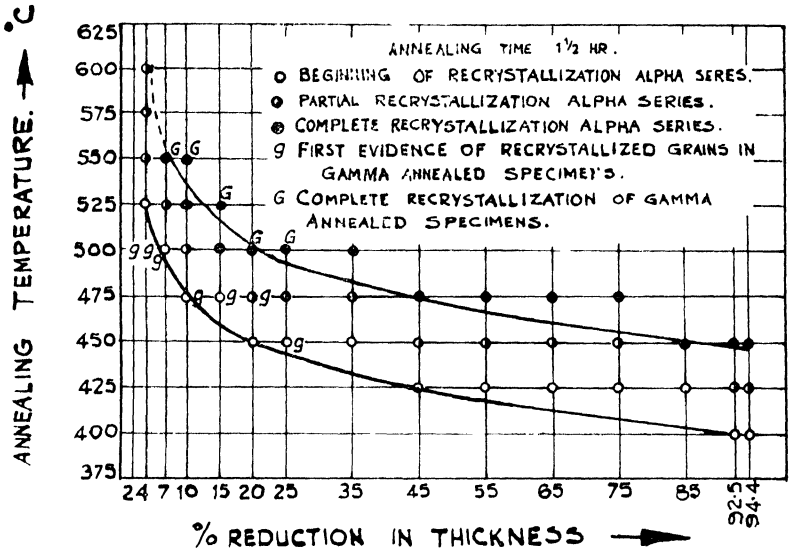

Fig. 13—Recrystallization temperatures are function of per cent reduction of uranium plate at room temperature. (Hayes, 1949).

formation of the grains existing prior to deformation (Figs. 14-a and 14-b). Even after heavy deformations below the recrystallization temperature, marked differences in grain size and orientation are evident after recrystallization (Fig. 14-c.) The differences in grain size between such bands are magnified when grain growth is less inhibited (Fig. 14-d). It is also probable that a large size will lead to non-uniform recrystallization after small reductions by rollings.

The differences in grain size between bands can be minimized by reducing the coarse grained billet in small steps with intermediate recrystallization between each step (Fig. 14-e). A fast beta treatment at some intermediate stage of rolling a rod is known to reduce the differences in orientation and grain size between bands (Fig. 14-f).

Preferred Orientation and the shape of grains in heat treated uranium: Deformation textures produced in uranium cannot be destroyed by annealing within the alpha range, instead a recrystallization texture is developed. However, it has been shown in the case of worked uranium rods that a fast or slow beta treatment results in an essentially random orientation.

If the transformation from beta to alpha is carried out at fast rates of cooling, as in water quenching, the resulting grain boundaries are markedly jagged in comparison to the relatively straight grain boundaries produced in more slowly cooled specimens. High purity specimens, water quenched from 1000°C and subsequently annealed at 650°C for 3½ weeks, have been found to contain relatively straight grain boundaries.

Fig. 14a.—50X. 89% reduction in area at 600°C.

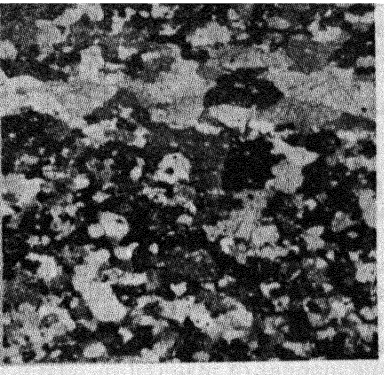

Fig. 14b.—50X. Same as (a) recrystallized 600°C—one hour.

Fig. 14c.—50X. 87% reduction in area at 300°C, annealed one hour at 475°C.

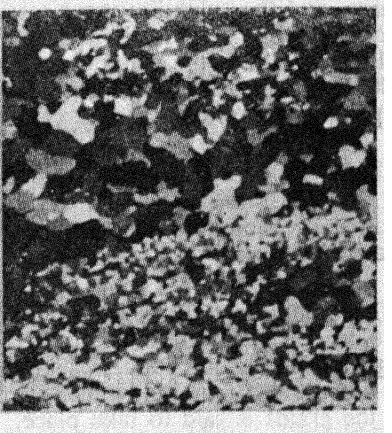

Fig. 14d.—100X. High purity rod, 90% reduction in area at 300°C, annealed two hours at 525°C

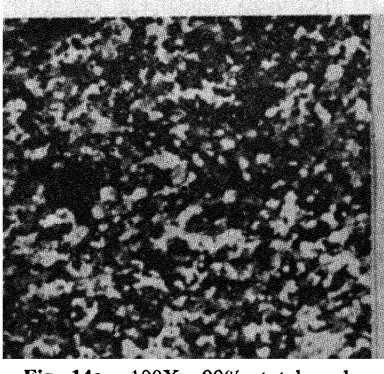

Fig. 14e.—100X. 90% total reduction in area at 300°C in five steps (15%, 30%, 30%, 48% and 48%) with intermediate recrystallization. Final anneal one hour at 475°C

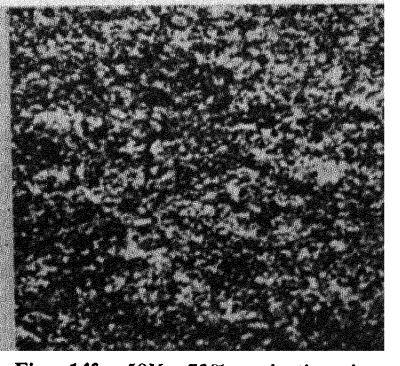

Fig. 14f.—50X. 73% reduction in area at 600°C, heated to 725°C for three minutes and water quenched, 47% reduction in area at 300°C and annealed one hour at 525°C

Grain size of heat treated uranium : The final grain size in heat-treated uranium depends upon several factors, such as the purity of the metal, the amount of strain produced before heating and the nature of heat treatment. The effect of these variables is discussed individually.

(a) *Effect of Impurities* : As most elements are insoluble in alpha uranium, very small weight percents produce a second phase. Consequently grain growth in uranium is extremely sensitive to differences in purity and to the heat treatment that affect the dispersion of the second phase. The inhibiting effect of the inclusions increases with their concentration. For the maximum grain size an optimum concentration exists. However, inclusions in finely dispersed form have a much greater inhibiting effect on grain boundary movement than the same amount of material in relatively large inclusions.

Most impurities are more soluble in gamma phase than in the alpha phase, and the solubility increases with increase in temperature. Consequently, if the metal is quenched to room temperature from some solution temperature in the gamma range, the solute precipitates during 300°C rolling and inhibits grain growth after recrystallization to a degree depending on concentration.

(b) *Effect of temperature* : Temperature has a significant effect on the grain size in uranium. Below 600°C a continuous type of grain growth is encountered. The effect of temperature on continuous grain growth decreases with increasing quantity of inhibitor.

In the range 600°-660°C, grain growth assumes a discontinuous nature. This is due to the coalescence of particles and the slightly higher solubility of impurities in the high alpha range, both resulting in a decreased inhibiting effect. In this temperature range, coarsening of the grains is said to take place. At the lower coarsening temperatures (600-625°C) the rate of coarse grain growth is not sufficient to prevent the formation of additional coarse grains or a gradual increase in matrix grain size. The maximum coarse grain size is usually attained at the highest annealing temperatures. The final grain size depends on how fast the grains, which are first to coarsen, grow before a general release in inhibition occurs, which again is primarily a function of temperature and the degree of inhibition.

(c) *Effect of time* : The effect of time depends on the inclusion dispersion, the as-recrystallized grain size and on the type of grain growth under consideration, i.e. continuous or discontinuous grain growth. For materials with reductions greater than 40 percent, there appears to be an equilibrium average grain size which progressively increases with temperature upto the coarsening range. The rate of approach to equilibrium decreases with increasing inhibition and with increasing time.

(d) *Effect of Strain* : Strain-anneal studies on impure tensile specimens which were machined from rods reduced 90% in area and recrystallized to a fine grain prior to extension have been carried out by E. S. Fisher (1). Fig. 15 shows the effect of per cent elongation at

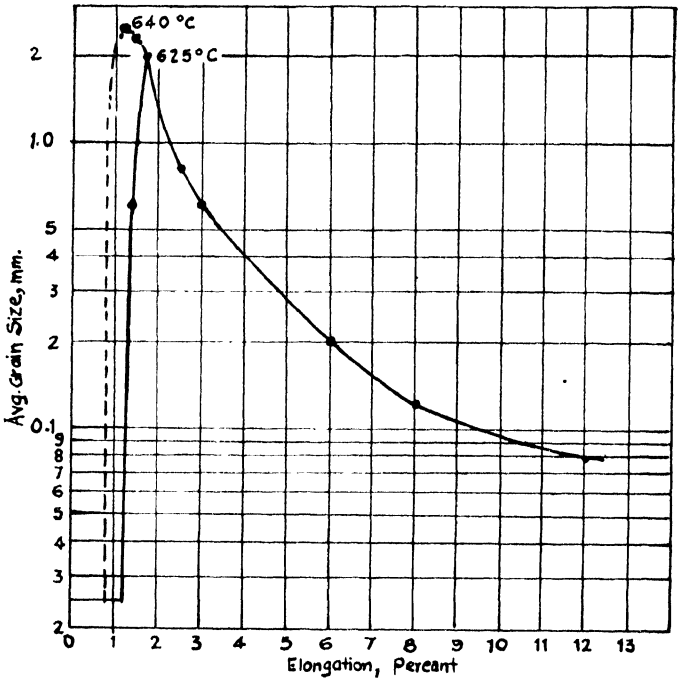

Fig. 15—Grain Size Vs. Strain in Impure Uranium. Increase of grain size with decreasing strain in elongated, tapered tensile bar annealed by heating at 5°C per hour to 625°C (solid line), and subsequently heated at 640°C for 45 hours (dotted line).

room temperature on the grain size produced after 45 hours at 640°C. The curve shows a significant effect of strain differences below 13% elongation, the effect increasing with decreasing strain. The sharp drop in the grain size occurring at approximately 1.2% elongation in this impure material (starting grain size approximately 0.012 mm.) suggests that recrystallization did not occur in specimens strained less than 1.2%. Other data indicate that strain differences above 40% reduction in area at 300°C have very little effect on the grain size after recrystallization.

(e) *Effect of transformation* : When specimens are uniformly cooled from beta to alpha range the grain size produced is primarily dependent on the rate of cooling through the transformation and, to a lesser degree, on the grain size prior to transformation. Faster rates of cooling, as in water quenching, and smaller grain sizes prior to transformation result in finer grain sizes in the transformed material.

But, the grain size prior to heating above the transformation temperature seems to have little effect on the final grain size.

Except in high purity uranium transformed at extremely slow rates of cooling, the grains present at room temperature contain sub-boundaries separating regions of slightly differing orientations. When the difference in orientation between subgrains becomes relatively large, the size of the subgrain is considered as the effective grain size.

Preparation of alpha uranium single crystals

(a) *Phase Change Method* : Columnar grains in uranium specimens can be produced by transforming beta phase into alpha, through a systematic temperature gradient. Fisher (1) has attempted the production of uranium single crystals by moving pencil-shaped specimens through a temperature gradient so that the point transformed first. Whereas, the tapered parts of the specimens contained equiaxed grains, the grains above this region were longer in the general direction of the temperature gradient. The number of grains at any section decreased with increasing distance from the pointed end. It was concluded that the number of columnar grains produced is primarily dependent on the size of the specimens and the purity of the material and is not significantly affected by the rate of movement of the specimen or the starting temperature. A single columnar grain occupying a complete cross section was successfully produced in impure rods of $\frac{1}{8}''$ or smaller diameters and in pure rods upto $\frac{1}{4}''$ diameters. But the single crystals produced by this method contained considerable substructure.

(b) *Strain-Anneal Method* : Attempts to prepare more perfect single crystals by strain anneal techniques have been unsuccessful. Cahn (2) proposed that the failure of this technique is basically due to the many twins which form during slight straining of alpha uranium. Because of the ease of twinning, too many recrystallization nuclei are formed during annealing for successful application of strain anneal techniques.

(c) *Grain-Coarsening Method* : This method, developed by Fisher (19), depends on grain coarsening induced by the gradual decrease in grain growth inhibiting influence of dispersed inclusions in a fine grained recrystallized matrix. The largest coarse grains are obtained when the concentration of fine inclusions is some optimum value, the primary recrystallized grains are of uniformly fine grain size, and the final annealing process carried out at the highest permissible temperature.

To prepare single crystals of round cross section it is necessary to create a radial concentration gradient, increasing from the axis, of the grain growth inhibiting inclusions. This is accomplished by diffusion of small quantities of silicon from the cylindrical surface. The rod is then quenched from the gamma phase and fabricated by a step reduc-

tion annealing schedule. Finally the rods are given a prolonged anneal in the high coarsening range i.e. 640-660°C. By this method, single crystals upto ¼″ dia. and showing complete absence of sub-structure, have been successfully produced.

Thermal expansion characteristics of Uranium

The linear thermal expansion co-efficients of anistropic alpha and beta uranium are dependent on the specific crystallographic directions under consideration. Consequently, dilatometric studies on polycrystalline samples, which take into account not only the voids and lattice defects, but also the macrofeatures such as preferred orientation present, are not of much use except for measuring average values for materials of known metallurgical history. Therefore, true co-efficients of linear thermal expansion of these two phases have to be either calculated from X-ray determinations of lattice parameters as a function of temperature, or determined by dilatometric measurements performed on single crystals. However, in the case of isotropic gamma uranium, the linear co-efficient of thermal expansion may be obtained by dilatometric studies on a polycrystalline sample.

Thermal expansion co-efficients of alpha uranium have been deduced from X-ray measurements of lattice parameters as a function of temperature by Bridge, Schwartz and Vaughan (20). Their data for the temperature range 27° to 640°C are plotted in Fig. 16 and 17. It is evident from Fig. 16 that the a and c-axis, in other words directions [100] and [001], show a uniform expansion and the b-axis or direction [010] shows a continuous contraction with increasing temperature. Since for most engineering applications the change in dimensions on heating above room temperature is desired, it is more practical to know the mean co-efficients between room temperature and the various temperatures through the alpha range. The mean co-efficient of thermal expansion in each of the three crystallographic directions and the volume co-efficient, as derived from the curves in Figs. 16 and 17 are listed in Table VI.

The thermal expansion characteristics of polycrystalline alpha uranium are profoundly affected by the type, temperature and degree of working given, or in short, by the type and degree of preferred orientation present in it. Representative values of the mean thermal expansion co-efficient along the fibre axis of uranium rods of various histories are given in Tables VII and VIII.

It is seen that increasing the amount of reduction in area and lowering the temperature of working causes the thermal expansion coefficient to decrease. This decrease in the co-efficient may be explained as follows : Increased per cent reduction in area and decreased temperature of working are known to cause an increase in the (010) preferred orientation. The [010] direction in alpha uranium has a negative thermal expansion co-efficient. Thus, an increase in the (010)

preferred orientation should result in a decrease in the mean thermal expansion co-efficient.

The mean therman expansion co-efficient of essentially randomly oriented polycrystalline material (beta treated) between 25° and 100°C is found to be about 16 x 10^{-6} units|unit|°C (1).

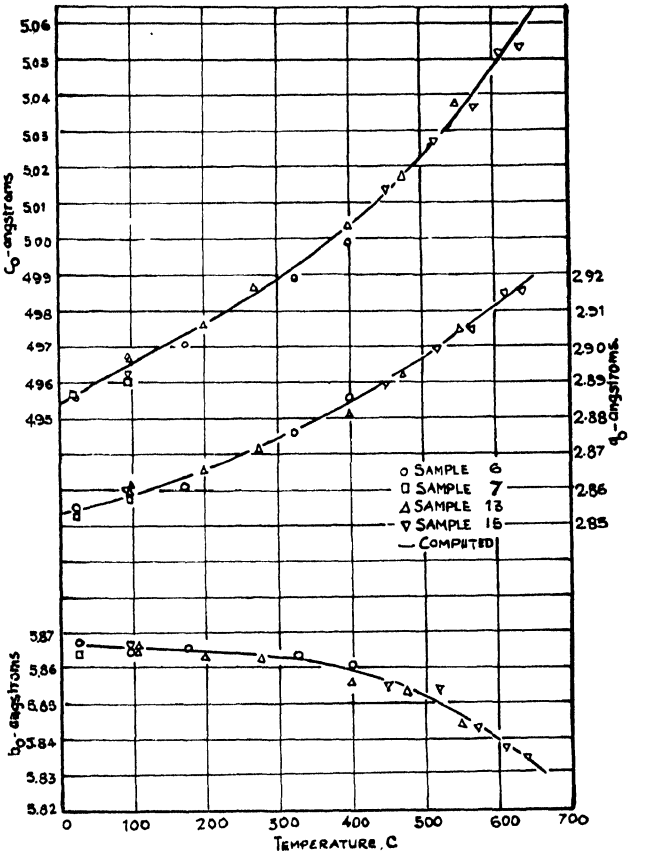

Fig. 16—Unit cell dimensions of ∝ Uranium as a function of temperature.

The thermal expansion co-efficients for beta and gamma uranium have been deduced by extrapolation of the lattice parameter values of 1.4 w|o Cr-U and gamma U-Mo alloys to zero per cent chromium and molybdenum respectively. The data of Thewlis (n) and Wilson and Rundle (q) are included in Table I.

Thermal cycling effects in uranium

When polycrystalline uranium is subjected to thermal cycling i.e. repeated heating and cooling, dimensional and structural changes take place.

The variables affecting thermal cycling behaviour of uranium may be classified into material variables and cycling variables. The material variables are degree of preferred orientation, grain size and the chemical composition.

On thermal cycling, randomly oriented material shows little over-all dimensional effect, but the internal microscopic deformation is increased and gain growth takes place. This causes surface roughening

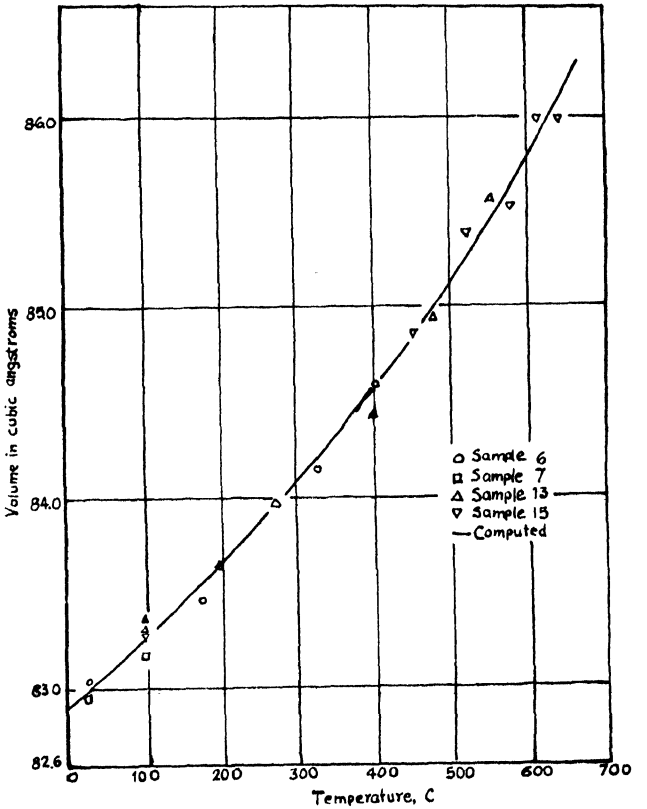

Fig. 17—Volume of ∝ uranium as a function of temperature.

as observed in cycled cast uranium. Preferred orientation on the other hand, caused over-all dimensional changes, but little effect on the microstructure[21]. The growth rate in uranium is known to increase with decreasing grain size. Chiswik[22] has shown that a decrease in grain size from 0.18 m.m. to 0.014 m.m. at constant reduction of area increased the growth in 700 cycles from 13.1 to 58.4%.

The thermal cycling behaviour of uranium is greatly affected by chemical composition. In impure material density decreases due to

Table VI—Mean coefficients of thermal expansion $\alpha m = \frac{Xt - X_{25}}{X_{25}(t-25)}$ as computed from the curves of figs. 16 and 17 per °C.

Temperature °C.	α a x 10^6	α b x 10^6	α c x 10^6	α v x 16^3
75	20.3	—1.4	22.2	45.8
125	21.7	—1.5	23 2	45.8
175	22.9	—1.7	22.9	45.8
225	23.5	—1.9	23.1	46.4
275	25.2	—2.0	23.2	47.7
325	26.5	—2.4	23.9	48.6
375	27.8	—2.9	24.8	50.3
425	29.5	—3.6	25.8	51.8
475	30.8	—4.7	27.3	53 6
525	32.5	—5 7	28.8	55.9
575	35.2	—7.1	30.9	57.8
625	35.9	—8.6	33.0	61.0
650	36.7	—9.3	34.2	61.5

Xt is the value taken from curves for a_0, b_0, c_0 and volume at various temperatures t and X_{25} is the cell dimension or volume at 25°C.

Table VII—Mean Thermal expansion coefficients of alpha uranium rods for varying fabrication treatments and per cent reductions in area

(R. M. Mayfield, ANL)

Treatment prior to final Rolling	Nominal Finish Rolling Temperature °C	Mean Thermal Expansion Coefficients (25° — 100°C) x 10^6 units/unit/°C.			
		0% Reduction	10% Reduction	45% Reduction	70% Reduction
600°C rolled–80%	300	13.42	10.16	8.62	8.94
600°C rolled–80% and beta treated	300	15.98	12.8	10.02	9.17
600°C rolled–80% and beta treated	600	15.86	14.9	13.39	12.71

Table VIII—Mean Thermal Expansion Coefficients of Alpha Uranium Rods for Varying Temperature of Rolling and Thermal Treatment, Uniform 75% Reduction in Area

(R. M. Mayfield, ANL)

Nominal Rolling Temperature°C	Mean Thermal Expansion Coefficients (25°-100°C)$\times 10^6$ units/unit/°C	
	As rolled	Recrystallized at Approximately 625°C
300	8.5	6.8
400	9.3	7.9
500	11.4	9.2
600	12.9	—
640	14.1	—

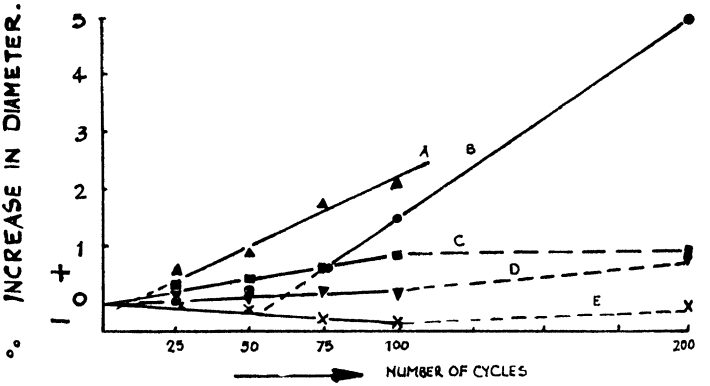

Fig. 18—Effect of alloy additions on the dimensional stability of uranium, Thermally cycled through the α -β phase transformation temperature[3]
A—Ca—reduced uranium.
B—U—2.08 at %V.
C—U—4.20 at % Mo
D—U—0.47 at %Mo.
E—U—0.55 at %Cr.

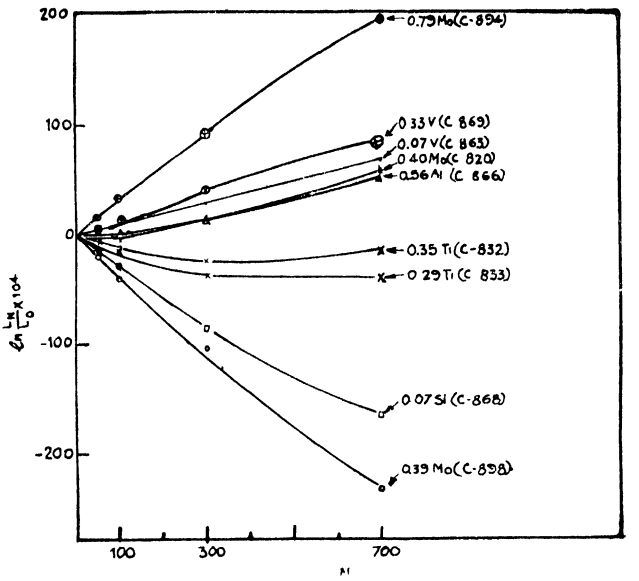

Fig. 19—Growth of specimens quenched from 710°-725°C.

the formation of voids. The effects of additions of alloying elements on uranium subjected to thermal cycling are shown in Figs. 18 and 19. White[23] has reported that dimensional changes on alpha thermal cycling can be kept at about 0.1% by the addition of 1.8 a/o Cr. combined with suitable heat treatment. According to Zegler and Chiswik[24] the surface roughening in uranium may be stopped by the addition of 2.0 w/o Mo.

The following cycling variables affect the thermal cycling behaviour of uranium: (a) rate of heating and cooling; (b) temperature level; (c) temperature range; and (d) holding time. Greatest growth rates are obtained with slow heating combined with fast cooling. Minimum growth rates result from the use of fast heating and slow cooling combination while intermediate growth rates are obtained with equal heating and cooling rates. For upper cycling temperatures above about 350°C, the greater the cycling temperature range, the greater is the growth. Also, for any given temperature range the higher the temperature level, the greater is the resulting growth. But little growth takes place if the upper temperature of the cycling range is kept below 350°C. Growth rate is also dependent upon the holding time at the upper cycling temperature. With increasing holding time above about 350°C the growth rate increases rapidly at first and then more slowly until it approaches a constant value. The higher the temperature, the shorter the time required for the growth rate to level off.

In addition to dimensional changes, a number of microstructural changes take place on thermal cycling uranium. These are (a) subgrain formation, (b) formation of voids, (c) crystallographic slip, (d) grain boundary migration, (e) grain boundary roughening and (f) surface roughening.

The boundary migration and subsequent subgraining observed upon cycling coarse grained uranium have been ascribed to the amount of disorientation between adjoining grains[25]. Deformation in coarse grains takes place mostly by slip, twinning taking only a minor part. The two slip systems revealed on cycling are (010)—[100] and (100)—[110], the former being the predominant one. The fine grained specimens deform by slip, grain boundary migration and some grain boundary slip. Beta treated material is known to show pronounced deformation upon cycling which may be a result of randomization, with the consequence of large disorientation between adjoining grains.

A number of mechanisms to explain the thermal cycling behaviour of uranium have been proposed on the basis of intergranular stresses developed as a result of anisotropy in the thermal expansion of alpha uranium. Of the various proposed explanations, several of the more acceptable include what is known as the "Bauschinger Effect" as a factor. Burke, Howe and Turkalo[26] have proposed a thermal ratchetting mechanism in which the intergranular stresses developed are relaxed by slip along the weaker grains i.e. grains having orientations slightly deviating from [010] direction. Mayfield's[25] work shows that the microstructure obtained as a result of deformation during thermal cycling is similar to that obtained in aluminium under creep conditions. Hence there is a possibility that growth on thermal cycling may be closely associated with Bettman's[27] creep relaxation phenomena. The various mechanisms proposed, however, are not in complete agreement with the available experimental evidence.

It is interesting to note that single crystals of uranium undergo no dimensional changes and show no evidence of internal deformation as a result of thermal cycling in the alpha temperature range.

The dimensional stability of uranium on thermal cycling may be obtained either with a strong can or by the addition of alloying elements. With the ratio of clad cross-sectional area to core cross-sectional area at 11%. Tantalum Jacket effectively restrains growth in uranium cylinders upto 800°C[28]. The addition of alloying elements like molybdenum and niobnium which stabilise the gamma phase also make uranium dimensionally stable.

Radiation Effects of Uranium

Changes in the structure and properties of uranium take place when it is irradiated with various types of radiations[29] to[32]. The most important of these are the ones encountered in the reactor operation[33].

All the parts of the reactor are subjected to radiation, but irradiation of uranium differs from these in two major respects.

1. The neutron flux to which uranium is subjected, is very large and this flux consists of neutrons of a wide range of velocities.

2. Uranium is subjected to the action of moving fission fragments. Since they are very heavy, they move over a very small distance, and thus are confined wholly to the fuel element.

When a particle moves through a lattice with an initial high velocity it affects the region surrounding its path in three ways. Firstly, it will ionise the surrounding atoms by the presence of charge on itself or due to the knocking out of electrons from the atoms. Secondly, it will collide elastically with the atoms coming in the path. These recoil atoms will in turn produce secondary collisions and so on. Thirdly, due to the inelastic collisions and weak elastic collisions, vibrations are set up in the region surrounding the path of the particle. This causes a temperature increase in this region. This region is called a "Thermal spike".

The ionisation effects are negligible in the case of solids and the elastic collisions produce most of the imperfections in the lattice. These imperfections can be vacancies, interstitials and dislocations. The path of a particle and various types of defects produced are shown in fig. 20[34].

Thermal spike is confined to a very small region around the path of the particle and temperature increases to 1000°K for a very short duration of about 10^{-11} sec.[32] when the energy of the fast moving particle fall below a certain value depending upon its atomic weight, its mean free path becomes equal to about the interatomic spacing.

This causes a large number of elastic collisions in a region containing about 1,000 to 10,000 atoms[34]. In this region local melting takes place and turbulent flow occurs. All the vacancies and the interstitials are annealed out. The main defects in these regions are the dislocation loops and misoriented regions. This region is called the "displacement spike".[34].

The types of defects described above are continuously produced in a fuel rod under operating conditions, and as such, its properties change with the production of these defects. But some of these defects anneal out, as for example, a vacancy and an interstitial may combine together or migrate to the grain boundary. Thus, the permanent effect of the imperfection will depend upon the degree of annealing out of the defects. If the rate of combination of the vacancies and the interstitials is less than the rate of their production, there will be a net increase in the number of vacancies and interstitials. At higher temperatures the annealing process takes place at a much greater rate.

Swelling : Besides the direct result of the collisions, there is another important effect of the irradiation. This is the production of impurity atoms due to the fission reaction. Some of these impurity atoms may alloy with uranium, however, the inert gas krypton is completely insoluble in uranium and its rate of diffusion is very low. This gas remains entrapped in the metal and causes increase in volume which is manifested in 'swelling' of uranium.

Effect of irradiation on properties : Most of the properties of uranium are affected by irradiation. A detailed discussion of these is given in the following references [29,30,31].

Surface of uranium roughens after irradiation. This becomes progressively worse as burnup increases and is dependent upon grain size and degree of preferred orientation.

Density of uranium decreases by about 0.5% for 0.1% burnup. The metallographic appearance of uranium after irradiation is similar to that obtained by coldworking.

The lines on the X—ray diffraction pattern are broadened after irradiation. The effect observed is similar to the broadening obtained after coldworking.

The mechanical properties of uranium are strongly affected by irradiation. It is embrittled severely even after fission of 1 in 10^5 atoms. It has been reported that 0.035% atom burnup at 120°C is sufficient to decrease the ultimate strength by ½, to double the yield strength and to practically destroy the ductility[30]. Hardness also increases after irradiation.

The electrical resistivity increases about 1% after 2 x 10^{-4}% of the total atoms have fissioned. Thermal conductivity decreases, approximately 5% after 0.1% burnup. The electrical resistivity and the elastic constants of the uranium rods are being very widely used for experimental purposes not only to study the nature of the radiation damage but also to study the nature of the imperfections in solids. The two important effects of irradiations are changes in dimentional stability and creep properties. These will be discused now in more detail.

Dimensional stability of uranium under the action of radiation[35, 33] : A single crystal of uranium, after irradiation elongates in the direction [010], shrinks in the direction [100], and remains unchanged in the direction [001]. This involves an extension of 5.0% after 0.1% burnup. For polycrystals the rates are higher and also with increasing degree of cold working, in otherwords with increasing degree of preferred orientation and decreasing grains size, the growth rate increases.

This growth of uranium has been explained on the basis of plasticity and/or diffusion mechanisms. The net result is that some atoms move preferentially along the [010] direction. It has also been postulated that both these mechanisms may be operating and that experiments to determine the effect of temperature and grain size on the growth rate of irradiated alpha uranium should help to determine as to which is the dominant process[36].

Creep properties of irradiated uranium[37] : In a normal polycrystalline metal, if a large internal stress is present, a slight amount of external stress will cause plastic flow in the grain. But this flow is restrained by the surrounding structure and before the overall deformation has exceeded the amount of elastic strain, equilibrium is reached. But in the case of uranium, since it grows constantly due to irradiation, this type of flow will not stop of its own accord and the material creeps slowly (10^{-7} cm/hr) at 100°C. This sort of irradiation behaviour has been encountered in actual practice.

Control of the radiation damage : The dimensional instability of uranium can be restricted and controlled by the following means:

1. Obtaining a finegrained and randomised structure. This is obtained either by choosing suitable fabrication techniques and heat treatments or by addition of alloying elements like Cr, Mo, Zr or by combining both these factors.

2. By changing the crystal structure of uranium to a simpler type which is stable under irradiation. This is achieved by alloying. A quenched molybdeum uranium alloy with 12% Mo gives gamma structure at room temperature and has good irradiation stability. Other suitable alloying elements are Nb and Zr.

3. By restraining the movement mechanically. If thicker cans are used the dimensions of the fuel rods are kept constant mechanically. For this it is necessary that changes in dimensions of U produce a tighter fitting[28].

Lengthening along axial direction and surface roughening of U specimens occur both under the action of thermal cycling and radiation. Since study of irradiation of uranium is of great importance and the procedures involved in these experiments are complicated and elaborate it is customary to evaluate the effect of irradiation by measuring the effect of thermal cycling[30].

But the mechanisms operating in these cases are not similar. The most important evidence for this is that irradiation effects are shown both by poly and single crystals, but thermal cycling effects are observed only for polycrystals.

Mechanical Properties of Uranium

The mechanical properties of uranium are affected by its mechanical and thermal history and also by the impurity content of the metal. This can be partly attributed to orientation and grain size changes brought about by various treatments.

The stress strain curve of uranium is characterised by a low proportional limit and marked hysteresis effects. According to McCutchan and Murphy [38] the proportional limit of uranium is less than 500 psi. The low proportional limit point to the impracticability of determining modulus of elasticity by static methods. Hence most of the accurate measurements of elastic properties have been done by dynamic methods [39,40]. Some of the results are shown in Table IX.

The yield strength at 0.1% offset can be increased 100% by means of cycling[41]. Resting between cycles of repeated tensile loading leads to a partial loss of the elasticity acquired during the previous cycling[38].

Tensile Properties : Alpha rolled uranium rods have different tensile properties in the rolling and transverse direction due to differences in orientation developed during rolling. The ultimate tensile strength and impact strength are greater in the longitudinal direction than in the transverse direction[42]. Increasing the temperature of working in the alpha range results in decreased tensile strength of uranium. Heat treatment of alpha rolled uranium in the beta range results in a decrease in tensile strength and increase in impact strength. The effects of various methods of fabrication and heat treatment on tensile properties of uranium are shown in table X[13].

The tensile properties of uranium are affected by the impurity content. Increasing the carbon content from 60 to 1250 ppm results in an increase in ultimate tensile strength from 23.2 to 33 tons/sq. in.

Hydrogen has a deleterious effect on the elongation of tensile specimens of uranium. The presence of 0.3 ppm hydrogen reduces the elongation of uranium from 32 to 10% at room temperature[44].

The strength properties of uranium decrease rapidly with temperature. Hot hardness measurements[17] show that there is a gradual decrease in hardness with temperature in the alpha range. On reaching beta range there is a sudden increase in hardness from 20 to 38 Brinell. Further increase in temperature leads to a decrease in hardness reaching a low value in the gamma phase, as shown in Fig. 12. Elongation measurements made at various temperatures show that gamma phase has the best ductility while beta phase has reasonable ductility.

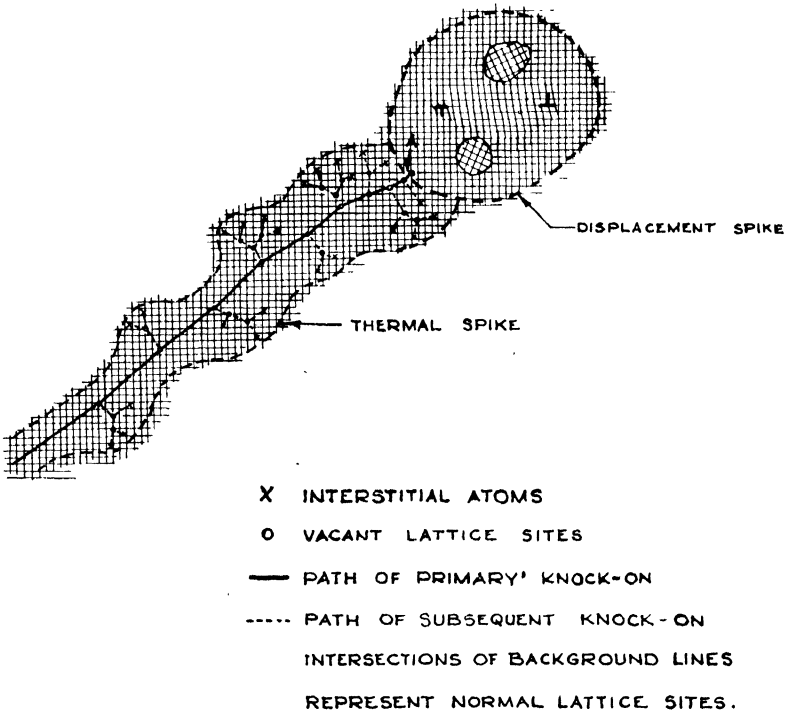

Fig. 20—Schematic diagram of situation resulting from passage of energetic knock-on atom through a solid.

Uranium exhibits a tensile transition i.e. transition from a slip type failure to semi cleavage type fracture at about room temperature. Marsh, Muehlenkamp and Manning[45] suggest that this transition is similar to that exhibited by many metals other than that of the face centred cubic type. The tensile transition in the uranium is affected by residual strain, strain rate, hydrogen content and to a lesser extent on heat treatment.

The creep strength of uranium depends on the composition and grain size. Variations in test temperature induce stresses between the grains. Variation in temperature of ½°C can produce stresses between individual grains of about 300 psi. These stresses make the accurate measurements of creep strength difficult and cause an apparent

Table IX—Elastic Properties of Uranium

Material and nature of test	Young's Modulus lb/in²	Shear Modulus lb/in²	Bulk Modulus lb/in²	Poisson's Ratio
Static Compression Average values	25.5×10^6	10.6×10^6	14.2×10^6	0.20
Dynamic				
Swaged	29.1×10^6	11.9×10^6	—	0.20
Gama extruded	29.3×10^6	12.0×10^6	—	0.21
Gamaextruded	30.3×10^6	12.1×10^6	—	0.25
as-cast	29.5×10^6	12.1×10^6	—	0.22
as-cast	30.0×10^6	12.1×10^6	—	0 25
average, dynamic	29.7×10^6	12.1×10^6	—	0.23

Table X—Room Temperature Tensile Properties of Uranium

Method of fabrication, Heat Treatment	Modulus of Elasticity psi x 10^6	Yield Strength 0.2% offset psi x 10^3	Ultimate Strength psi x 10^3	Elongation Per cent
as cast	24	28	56	4
Rolled—570°F				
annealed—1110°F	—	43	111	7
annealed—1290°F	—	25	64	9
Rolled—1110°F				
annealed—1110°F	—	26	88	14
annealed—1290°F	—	25	62	6
rolled—1020°F	25	31	96	11
rolled—1020°F				
annealed—1560°F	21	26	57	5
quench—1335°F	24	36	84	9
quench—1335°F anneal—1020°F	22	32	90	12
extruded				
2:1 ratio, 390°F	22	52	127	6
2:1 ratio, 750°F	24	46	125	11
8:1 ratio, 750°F	18	32	103	18
14:1 ratio, 1110°F	16	28	96	20

increase in the creep rate of uranium which is most probably due to the plastic deformation produced during cycling to room temperature from the test temperature. The creep strength of uranium can be improved by the addition of Ti, V and Th in amounts less than 1 a|o[17].

Alloys of Uranium

Uranium exists in three allotropic modifications. In the alpha and beta state uranium has a complex structure. This leads to low solid solubilities of other elements in α and β uranium. Gamma uranium has a body centered cubic structure and has a valency of six. The solid solubilities of various elements in gamma uranium are determined by atomic size factor and electrochemical factor. The atomic size

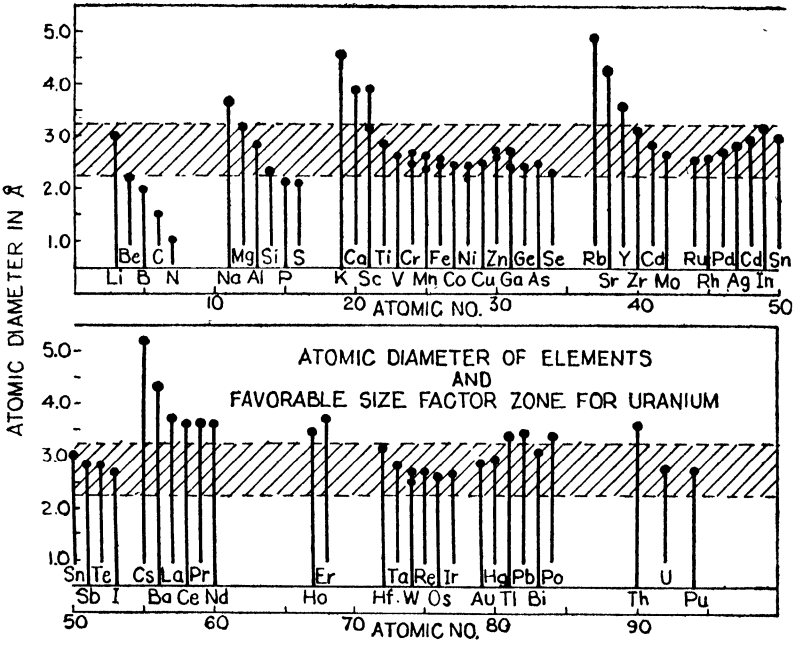

Fig. 21

factor is graphically represented in Fig. 21. From this figure one can see that extensive solid solutions should be formed with Ti, Zr, Nb, Mo, Pu, Ta and W. But Ta and W dissolve only to a limited extent. Ionic diameter can also be used as a criterion for obtaining the size factors and Buzzard[46] has suggested that ionic diameter serves as a better criterion than atomic diameter.

Binary diagrams of uranium : Binary diagrams of uranium can be classified into (1) Systems with intermetallic compounds and (2) Systems without intermetallic compounds.

Of the systems without intermetallic compounds U-Cr (Fig. 22) characterises the systems possessing eutectic and limited solid solubility.

Zr, Ti, Nb and Mo possess extensive solid solubilities in uranium (Figs. 23 to 26). Zr, Ti and Nb form a continuous series of solid

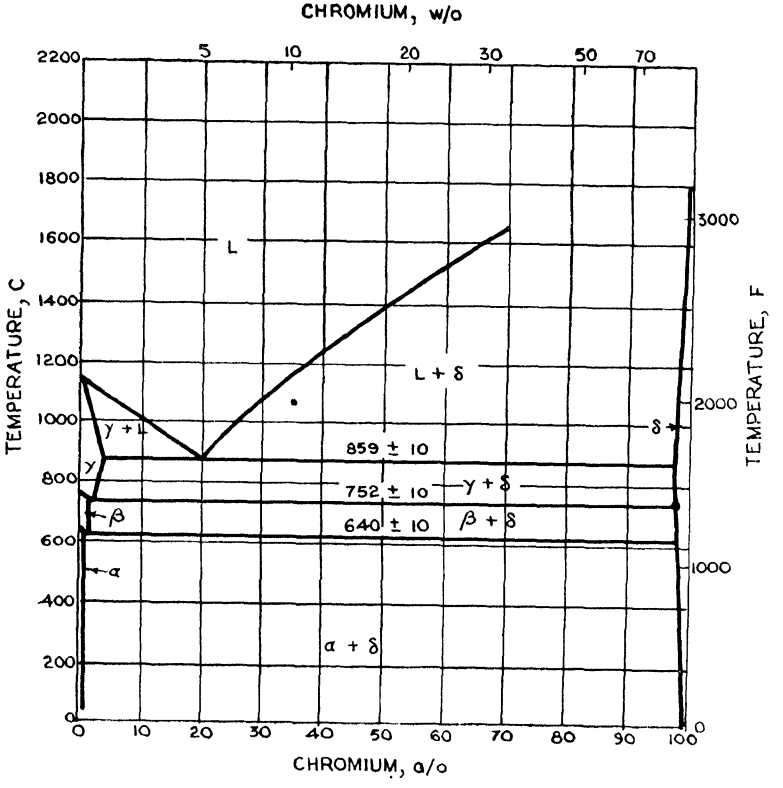

Fig. 22—Uranium-chromium system.

solutions with gamma uranium. The gamma phase decomposes to form an intermediate phase in Zr, Ti and Mo systems. In the case of Nb the gamma phase decomposes to another gamma phase of different composition.

Typical of the systems with intermetallic compounds are uranium—aluminium and uranium-silicon. (Figs. 27 and 28). Aluminium forms three intermetallic compounds UAl_2, UAl_3 and UAl_4. The formation of UAl_4 must be prevented when using Al as a canning material since UAl_4 does not from an adherent layer either with uranium or aluminium.

The first long period of the transition metals form compounds of

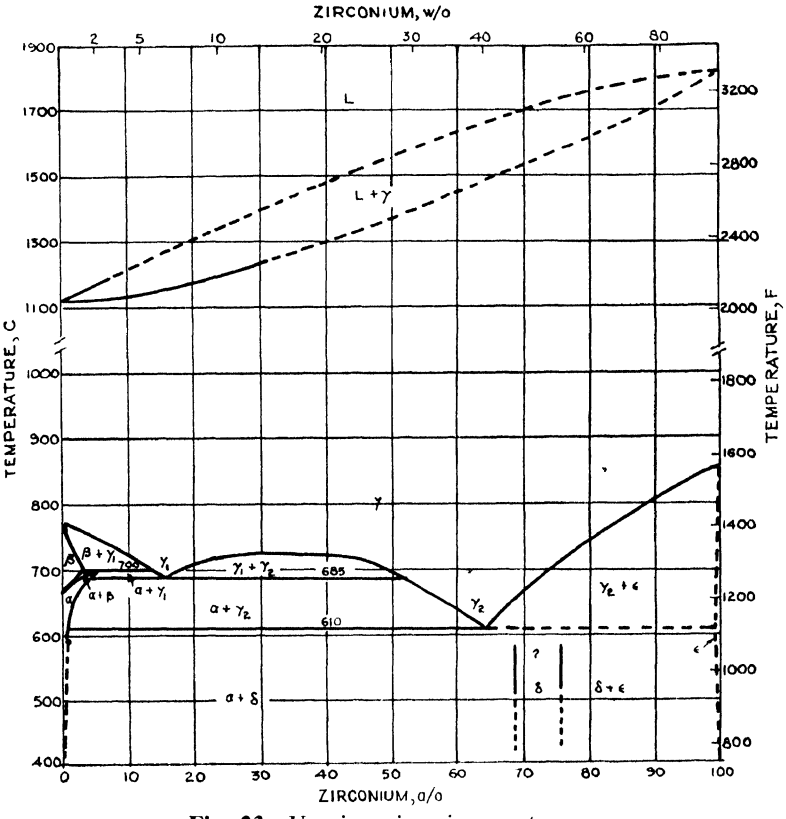

Fig. 23—Uranium-zirconium system

the type U_6X and UX_2 laves phases. The second and third long periods of the transition metals do not parallel the behaviour of the first except that in the third period the laves phases UOs_2 and UIr_2 with structures similar to UFe_2 and UCo_2 are formed.

Practical Applications: For economic power generation it is of advantage to raise the temperature of operation of a reactor. Hence interest is focussed on uranium alloys possessing high temperature strength and good corrosion resistance. Small additions of Al and Si to uranium improve the mechanical properties of uranium by the formation of intermetallic compounds dispersed uniformly in the matrix. Increasing additions of Al and Si cause an increase in the amount of brittle intermtallic compounds leading to lower corrosion resistance and elongation properties.

Small addition of Cr, Mo, Nb and Zr improve the mechanical properties by solid solution hardening. But for good high temperature strength and irradiation stability it is necessary to add large amounts

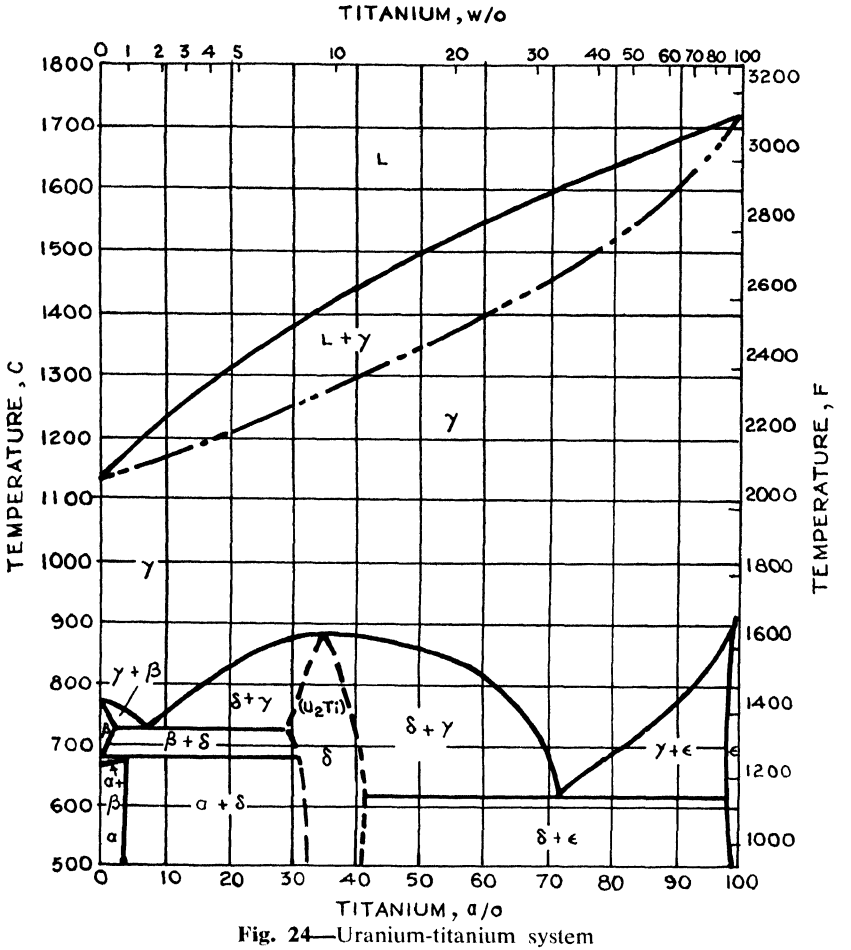

Fig. 24—Uranium-titanium system

of solid solution forming elements Mo, Zr, Nb and Ti. The effects of additions of alloying elements of tensile properties of U are shown in Table XI, XII and XIII.

The corrosion resistance in high temperature water is improved by the addition of gamma stabilising elements like Mo and Nb. These are sometimes prone to "discontinuous cracking", i.e. failure due to the formation of uranium hydride phase.

'Epsilonisation' of U-3.8 w|o Si alloy i.e. heating at 800°C for 168 hrs. to convert the cast α-μ and U_3Si_2 structure into U_3Si results in good corrosion resistance to high temperature water and irradiation stability. But the alloy fails when irradiated in high temperature water.

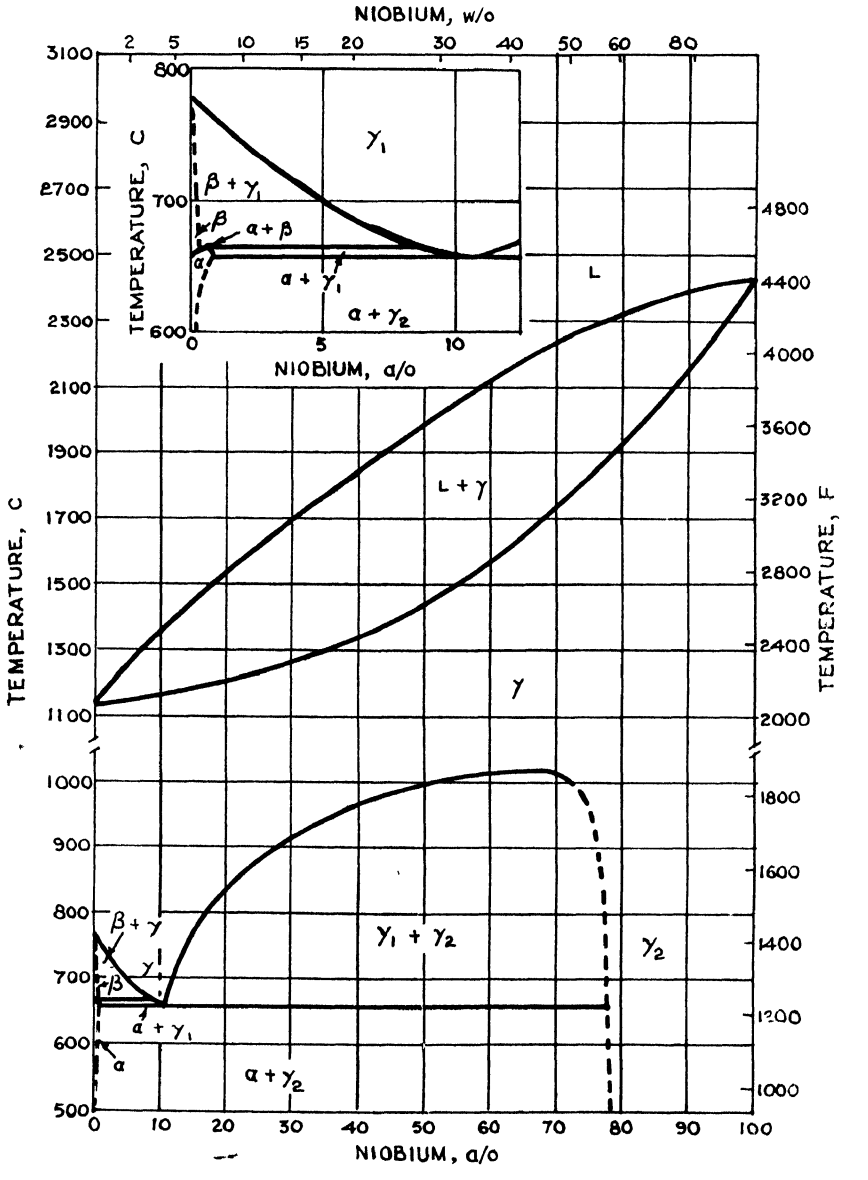

Fig. 25—Uranium-niobium system

Transformation Kinetics in Uranium Alloys

The beta and gamma phases retained at room temperature by the addition of alloying elements like chromium and molybdenum are metastable and change to the equilibrium phase when kept at lower

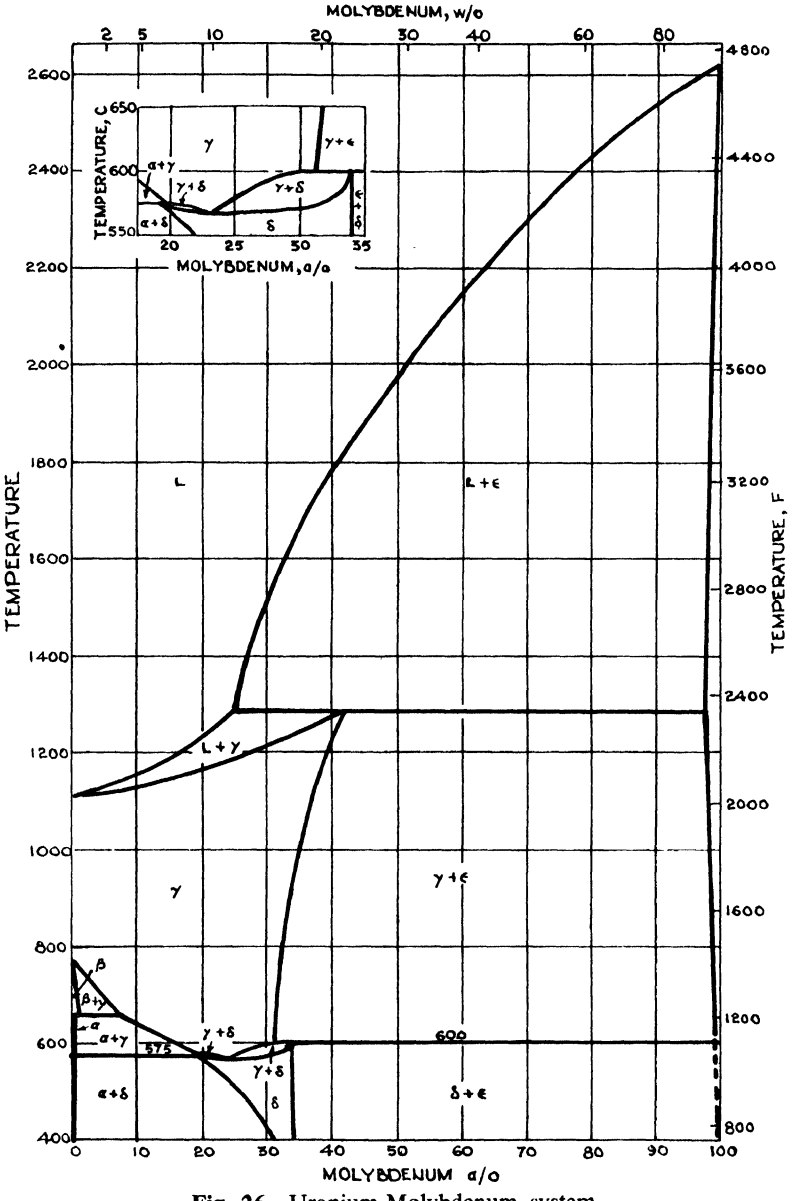

Fig. 26—Uranium-Molybdenum system

temperatures. Due to the potential use of uranium alloys in reactors, their TTT diagrams are of considerable interest to the nuclear metallurgist.

Uranium-chromium alloys: White Jr. [47] has reported the trans-

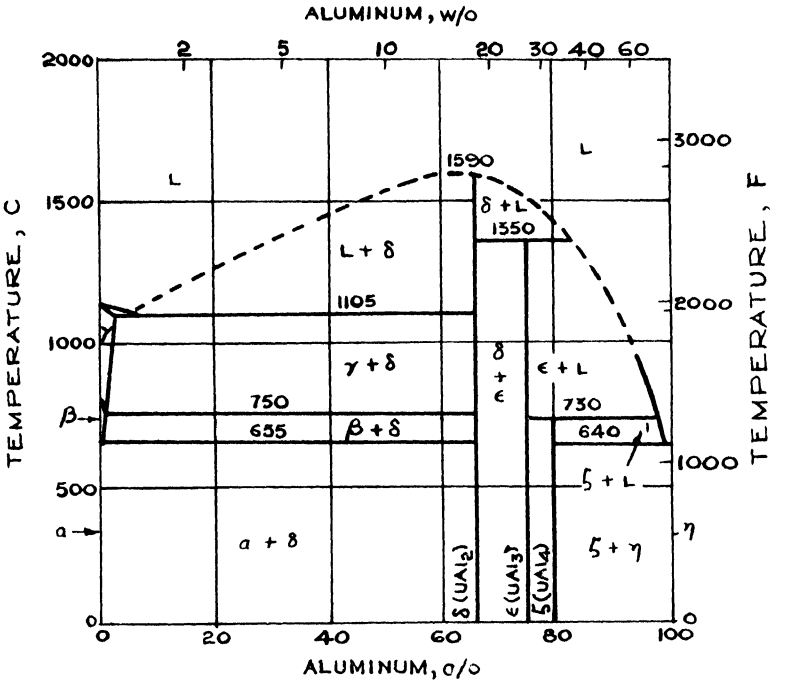

Fig. 27—Uranium-aluminum system

formation kinetics of 0.3, 0.45, 0.6. 1.8 and 4 a|o chromium-uranium alloys.

The TTT diagrams of U-Cr alloys are of the double 'C' type indicating that the transformation at higher temperatures is controlled by the rate of diffusion of chromium in β uranium, while transformation at lower temperatures takes place by a diffusionless mechanism. Increasing the chromium content in solution in beta phase decreases the

Table XI—Tensile Properties of Uranium and some Alloys at 500°C

Analysis Wt. %	Grain size mm	Ultimate tensile strength (tons|sq. in)	0.2% yield strength (tons|sq. in)	Elongation on 2 in.(%)	Reduction of area (%)
Base Uranium	>0.118	5.0	3.7	26.0	78
(<0.01 C)		5.6	3.5	29.0	87
U-0.10 Chromium	0.057	14.1	10.4	24.5	57
(<0.01 C)		11.6	6.8	25.5	85
U-0.42 Chromium	0.025	17.3	11.0	23.0	82
(<0.01 C)		16.6	10.6	23.0	82
U-1.11 Zirconium	0.033	19.4	14 0	11.3	61
(<0.01 C)		27.1	21.5	21.0	94
U-2.21 Zirconium	0.009	20.6	18.5	18.0	85
(<0.01 C)		23.4	20.1	24.0	94

Table XII—The Effect of Molybdenum Additions on the High Temperature Tensile Strength of Uranium

Temperature (°C)	Property (U.T.S. tons/sq. in) Elongation, per cent on $4\sqrt{A}$ gauge length	As cast Mg-reduced Uranium	Molybdenum content (weight %)						
			Alloys of vacuum H.F. cast into graphite; forged, rolled and heat treated 900°C for 7 days water quenched						Extruded
			2.2	4.6	6.6	7.8	10.0	10.9	10.9
100	U.T.S.	—	36.0	—	—	—	—	—	80.0
	Elongation	—	—	—	—	—	—	—	5.6
200	U.T.S.	20.2	—	38.4	42.7	38.4	37.0	—	73.5
	Elongation	24.0	—	12.0	4.0	6.0	0.5	—	6.5
300	U.T.S.	15.3	—	—	42.8	—	—	—	64.0
	Elongation	30.0	—	—	6.5	—	—	—	4.5
400	U.T.S.	7.1	—	32.7	43.5	35.6	26.1	25.5	56.6
	Elongation	28.0	—	5.0	3.0	9.0	1.0	0.5	3.0
500	U.T.S.	—	—	—	—	—	—	—	—
	Elongation	—	—	—	—	—	—	—	—
600	U.T.S.	3.7	—	12.4	—	25.0	12.9	9.4	—
	Elongation	42.0	—	7.0	—	5.0	—	0.5	—
700	U.T.S.	5.8	2.4	—	2.6	—	—	10.6	—
	Elongation	13.0	66.5	—	70.0	—	—	1.0	—
800	U.T.S.	—	1.8	—	1.1	4.1	4.1	6.6	—
	Elongation	—	81.0	—	94.0	69.0	30.0	6.0	—

Table XIII—The Tensile Creep Properties of some Binary Alloys of Uranium at 500°C 2 tons/sq. in.

Nominal Composition (atomic %)	Metallurgical condition	Average grain dia. (mm)	Time in hours for specified percentage creep strain					Minimum secondary creep rate (in/in-hr)
			0.1	0.2	0.5	1.0	2.0	
U-½ Ti	As cast	0,83	>1,000	—	—	—	—	$<0.2 \times 10^{-6}$
U-2 V	As cast	0.10	500	1.000	—	—	—	0.2×10^{-6}
U-½ Th	As cast	1.0	100	—	—	—	—	0.2×10^{-6}
U-1 Th	As cast	—	20	250	—	—	—	0.4×10^{-6}
	Beta-quenched	1.3	25	200	—	—	—	0.6×10^{-6}
U-4 Al	As cast	—	20	80	1,900	—	—	0.8×10^{-6}
	Beta-quenched	0.50	—	20	150	550	1,500	12×10^{-6}
U-½ Ge	As cast	0.80	—	20	100	540	—	4×10^{-6}
	Beta-quenched	0.2	—	—	15	40	110	135×10^{-6}
U-2 Ge	As cast	0.80	—	15	86	320	1,100	5×10^{-6}
	Beta-quenched	0.40	—	10	60	—	—	38×10^{-6}
U-2 Fe	As cast	1.06	—	20	40	120	580	30×10^{-6}
	Beta-quenched	0.3	—	5	10	20	60	700×10^{-6}
Mg-Red. Uranium	Beta-quenched alpha annealed	0.33	10	31	95	195	380	54×10^{-6}

transformation rate resulting thereby in the retention of the beta phase at room temperature. The presence of undissolved second phase tends to hasten the transformation. Extrapolation of the curves to 0 o/o Cr indicates that the $\beta \rightarrow \alpha$ transformation in pure uranium is diffusionless.

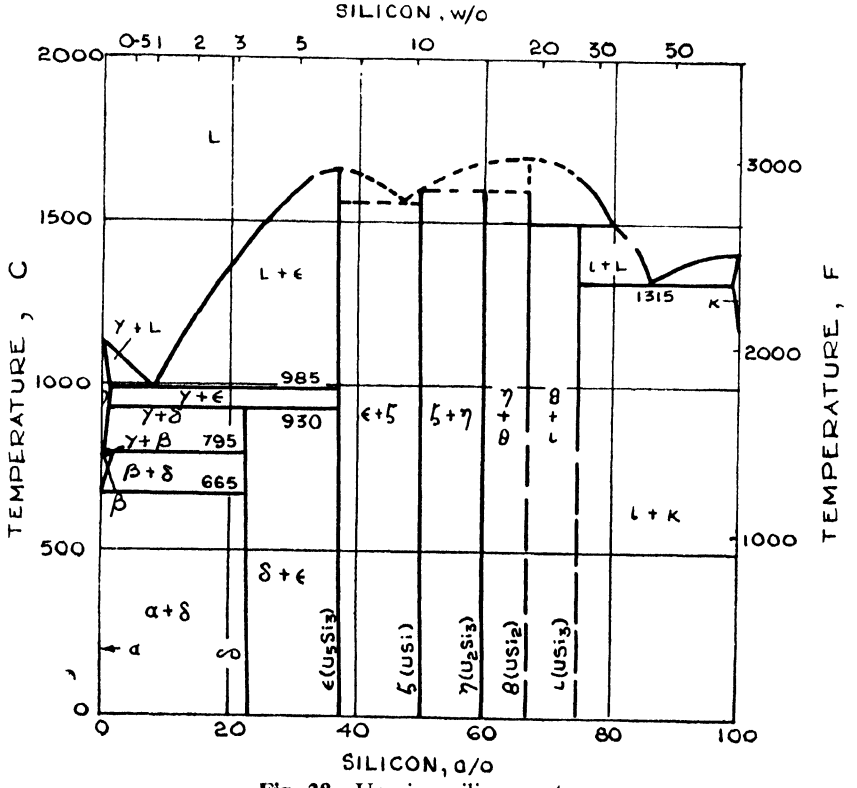

Fig. 28—Uranium-silicon system.

Uranium-molybdenum alloys : Transformation kinetics of uranium molybdenum alloys have been studied by various investigators. TTT diagrams of uranium alloys containing 0.5 and 1 w/o moylbdenum are also of the double 'C' type as shown in Figs. 29 and 30[48]. The nose for the 0.5 and 1 w/o Mo occurs at 550°C and 600°C respectively. Quenching the 0.5 w/o alloy from the high temperature gamma phase results in martensistic $\alpha + \beta$ structure. Quenching from beta phase with about 0.2 w/o Mo results in retaining the beta phase at room temperature.

In the 5.4, 8, 10 and 12 w/o Mo-U alloys gamma phase is retained on water quenching[49]. Transformation of the gamma to $\alpha + \epsilon$ phases is initiated at the grain boundaries and grows inwards to consume the gamma grains. The nose of the curve for 5.4 w/o is at 550°C and

0.1 hr. Increasing amounts of molybdenum increase the time taken for initiation of transformation. At 400°C and below, transformation was not complete for 5.4, 8, 10 and 12 w/o Mo even after 1000 hours. The results indicate that the transformation is controlled by the tendency of the alloy to order and also by the rate of diffusion.

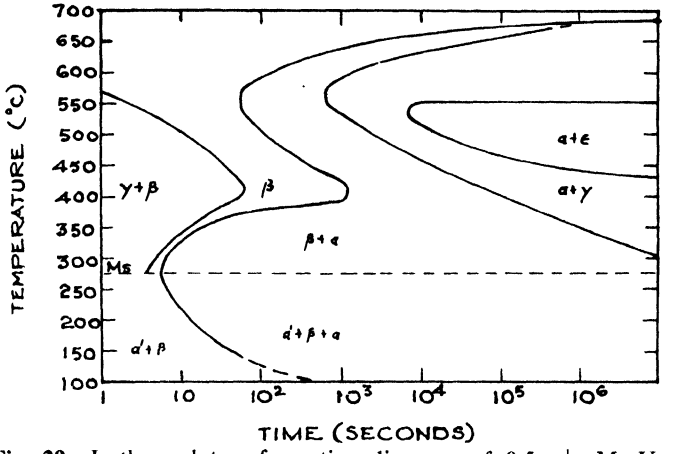

Fig. 29—Isothermal transformation diagram, of 0.5 w|o Mo-U.

Transformation kinetics of U-8% Mo-1% Pt. U-8% Mo-1.5% Nb and U-8% Mo-3% Nb have been studied by Van Thyne and Mcpherson[50]. TTT diagrams indicate that the initiation of transformation

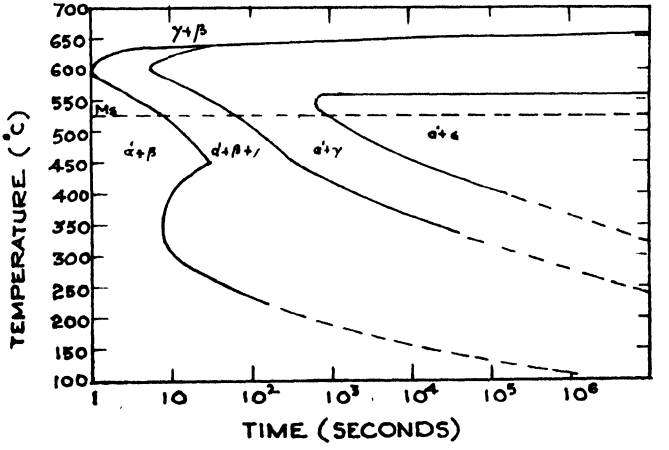

Fig. 30—Isothermal Transformation diagram of 1.0 w|o Mo-U.

takes place earlier at 500°C in the U-8% Mo 3% Nb alloy than in the other two alloys. But below 400°C the 8% Mo-3% Nb is more stable than the other alloys.

Uranium-niobium alloys : Transformation kinetics of U-10% Nb and 20% Nb have been studied by Van Thyne and Mcpherson[50]. The gamma phase transforms to $\alpha + \gamma_2$ phases. The nose of the transformation curve for 10 and 20 w/o Nb exist at 0.2 and 10 hrs. at 550°C as shown in Fig. 31. The hardness data for 10% Nb indicate that an increase in hardness occurs after short annealing times and

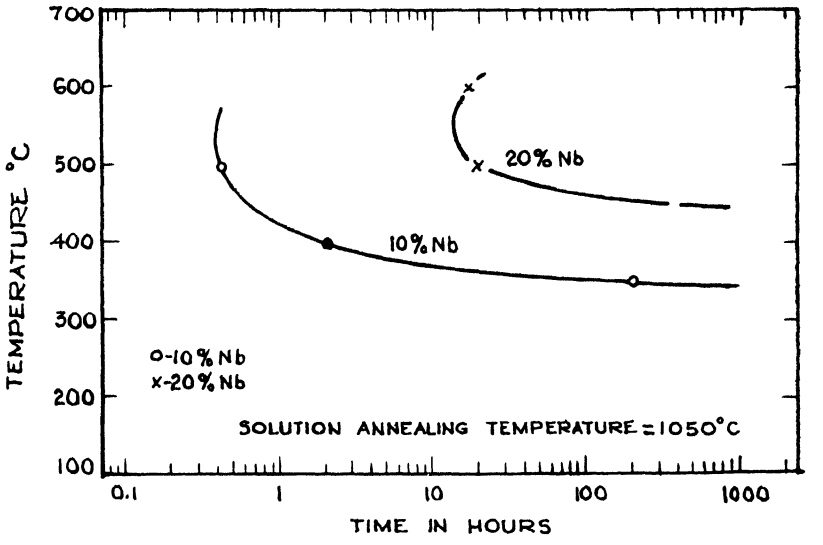

Fig. 31—TTT diagrams illustrating initial resistivity decrease for U-Nb Alloys.

before any precipitation is observed at the lower temperatures as seen in Fig. 32. The increase in hardness at lower temperatures might be caused by precipitation hardening.

Below 350°C no transformation was detected in the U-20 w/o Nb alloy after 1000 hours. This shows the incresasing sluggishness of the transformation with increasing niobium content.

Solid State Reactions between Uranium & Canning Materials

To protect uranium fuel rods from the corrosive action of the reactor coolants and to avoid contamination of the coolant with the fission products in the fuel rods, it is necessary to separate the uranium rods from the coolant. This is accomplished by totally enclosing, or canning the fuel rods in tubes of some suitable material. The suitability of the canning materials is dependent upon the following points[51] :

1. Low cross section for thermal neutron absorption.
2. Good resistance to coolant attack.

3. Compatibility with uranium under operating conditions.
4. Good ductility, thermal conductivity and adequate strength.

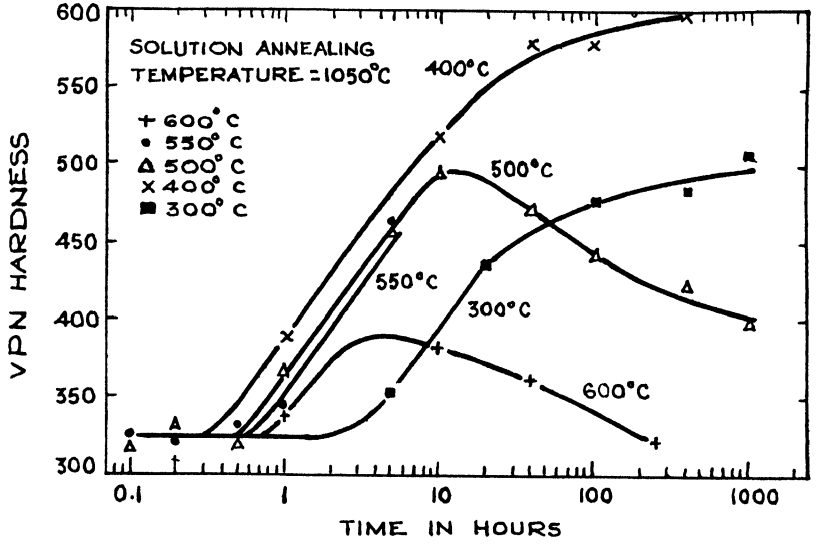

Fig. 32—Hardness data for an isothermally transformed U-10 wt % Nb Alloy.

For a thermal reactor the most suitable materials are Be, Mg, Zr and Al. Some of their properties are given below[52] :

Table XIV—Some Physical Properties of Canning Materials

	Be	Mg	Zr	Al	Nb
Thermal Neutron C.S. 10^{24} σ abs. Cm^2/Cm^3.	1.23	2.54	7.65	13	59.9
Thermal conductivity at 125°C ; BThU/Cft°F	80.64	95.76	10.08	133.56	32.76

Compatibility of the canning materials under reactor conditions is one of the most important property and necessitates study of the solid state reactions between uranium and the canning materials. Such studies have been carried out only to a limited extent and only for a few metals, of which Al, Zr and Mg are the more important cases.

U-Al : From the phase diagram (Fig. 27) it will be seen that in this system three intermetallic compounds UAl_2, UAl_3 and UAl_4 are formed. Of these UAl_2 and UAl_3 are adherent but UAl_4 cracks to powder and gives bad contact zones. Thus its presence is undesirable in the diffusion zone. Reaction between aluminium and uranium starts at about 250°C and the rate of reaction increases rapidly with temperature[53].

The extent of solid state reactions can be reduced by (a) coating U-rod with an adherent inert film of some material e.g. brazing U-rod to the can by means of Al-Si eutectic alloy or (b) by interposing an anodic coating on the inside of the Al tube.

U-Zr : Marsh & Disselhorst[54] have studied the solid state reactions between U and Zr at temperatures varying from 300°C to 1050°C and for times upto 1812 hours. They give two different equations for the rate of diffusion below and above 600°C. This temperature seems to mark the change of the type of mechanism of solid state reaction. Zr is compatible with U at temperatures relatively higher than those for Al.

U-Mg : Magnesium is totally inert towards uranium; but since it is not weldable to U, alloys of Mg have been developed[51]. These are called as "Magnox" alloys. The "Magnox C" alloy with a nominal composition of 1.0% Al, 0.4% Be and 0.05% Ca is found to be suitable canning material for use in reactors employing CO_2 as a coolant.

For high temperature reactors, stainless steel etc. are also used and some informative data for these is given in the table below[55].

Table XV—Data on Diffusion Couples

Couple	Temp.°C	Time to penetrate 0.01"	Useful range °C
Al—U	300	90 days	250—450
Fe—U S.S.—U	625	1 year	600—700 500—700
Zr—U	740	45 days	600

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Discussions

Dr. R. Caillat, (*France*): The excellent account of Dr. Tangri is certainly highly informative. However, I would like to complete it with a few results obtained in France : the behaviour of uranium in thermal cycling is highly improved if the metal is constrained by a mechanically resistant sheath. This has some important applications in the fabrication of fuel elements. It is precisely in this range that Mr. Stohr has studied the mixed U-Zr extrusion which forms the subject of his lecture.

On the other hand, concerning the swelling, I would like to report a hypothesis of Mr. Salesse, Head of the Department of Metallurgy and Applied Chemistry, which seems to me specially interesting. Theorists have shown, particularly at Harwell, as stated by Mr. Wyatt, that the accumulation of gases from fission in the cavities at the interior of the metal necessitates the initial presence of a pore of diameter *greater* than a certain critical value.

(a) We will especially observe this swelling if we start with an uranium richer in hydrogen, capable of forming these micro-bubbles, around which the gases from fission will collect. This brings up the consideration of the vacuum melting of the uranium for fuel elements under a new point of view.

In France, this melting is conducted in such a manner that the hydrogen content of uranium with which G_1 is charged, for example, is lower than 1 ppm.

On the other hand, the casting under vacuum leads to ingots which can be directly sheathed, without machining the surface.

BRITISH PRACTICE IN URANIUM METAL FUEL ELEMENT MANUFACTURE

*By L. M. Wyatt**

Production of Uranium Metal

The uranium metal which has been used in Great Britain so far for the manufacture of fuel elements has been made by the reduction of uranium tetrafluoride by magnesium or calcium to form a billet (fig. 1). Some experimental work has been carried out on the reduc-

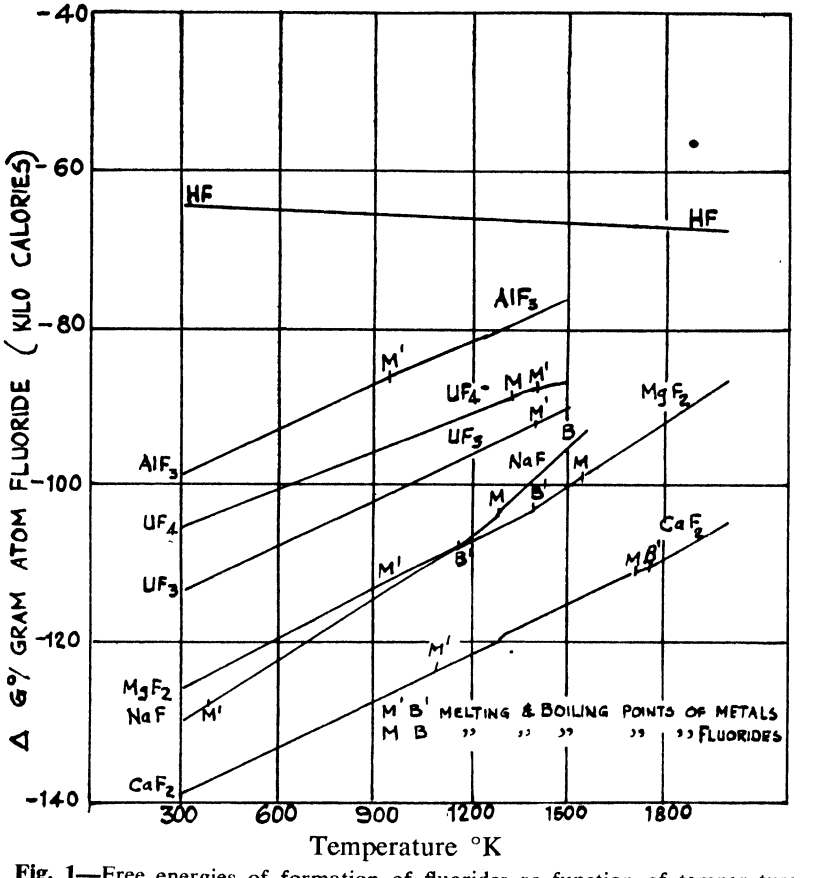


Fig. 1—Free energies of formation of fluorides as function of temperature.

tion of UO_2 by calcium (fig. 2) to form spherical uranium powder which can be made into fuel elements by powder techniques; but this

* U.K. Atomic Energy Authority, Risley.

method has not so far proved economic compared with the more conventional casting and metal working techniques associated with metal billet production by the fluoride route. The method of calcium reduction which was originally employed has been described by several authors (see Hedger 1). The technique consists basically of preparing a tamped or partially pressed and sintered calcium fluoride mould (fig. 3) which should, for a satisfactory reduction, be as dry

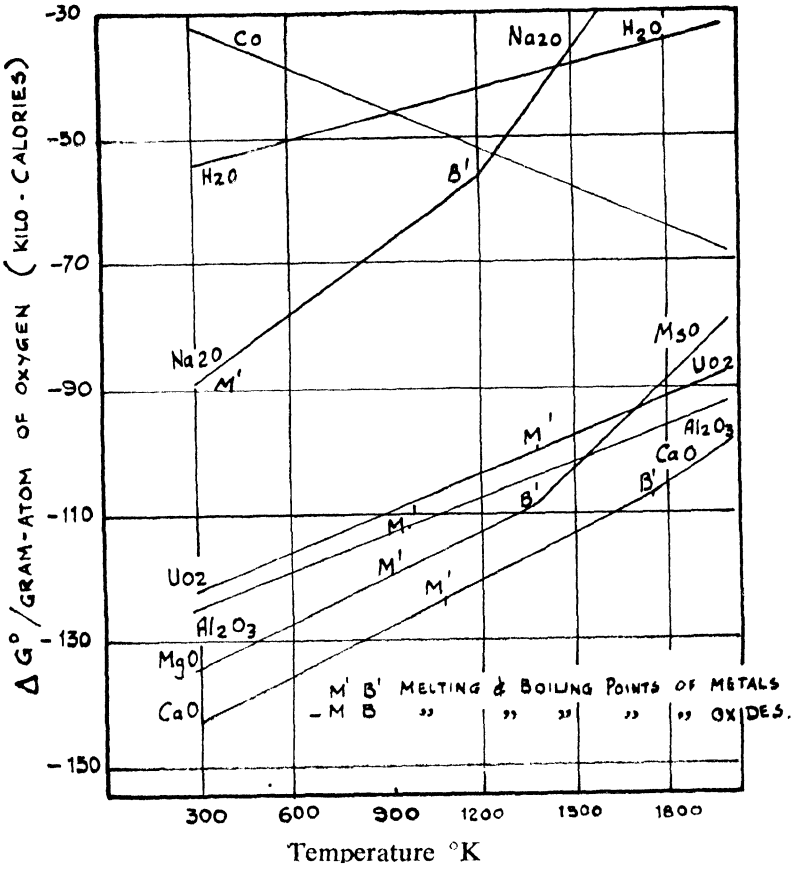


Fig. 2—Free energies of formation of oxides as a function of temperature.

as possible. The UF_4 is mixed with calcium which should be free from nitrogen and magnesium. Calcium produced by distillation and deposited in the vapour phase is the most satisfactory form. This takes the form of a fern which can easily be broken up by a conventional type of jaw crusher. The reaction can take place either in atmospheric air or in argon. For the latter technique the charge must be placed in a container which can be evacuated before argon is added so that the argon penetrates throughout the charge. The reaction is

initiated by the use of a chemical or electrical type fuse. Potassium nitrate and lactose, magnesium ribbon buried in magnesium powder and sodium peroxide have been found satisfactory. The uranium is melted by the heat evolved during the reaction and runs to the bottom of the mould which is shaped to produce a billet of the required section.

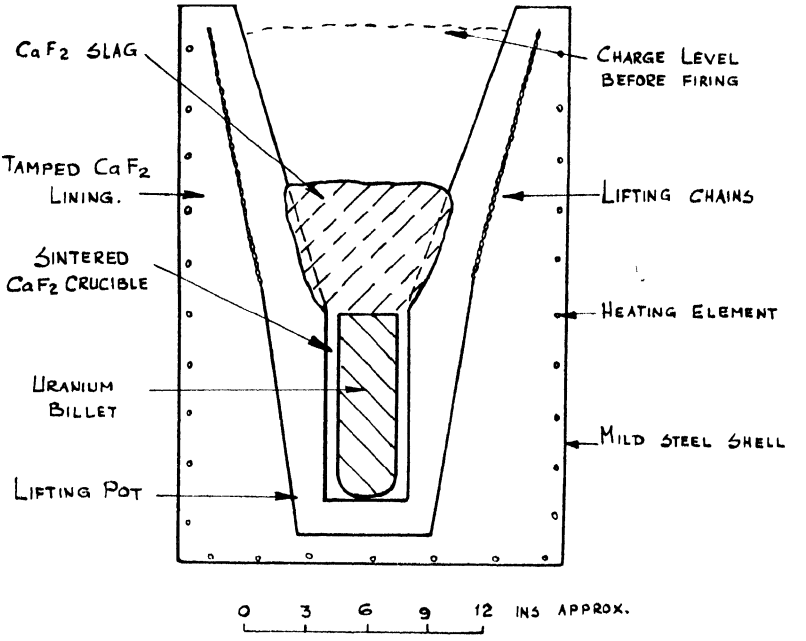


Fig. 3—Calcium—UF_4 reduction vessel after reaction (40 lb uranium approx.)

After cooling, preferably in argon, the mould is inverted, the calcium fluoride knocked out mechanically and the uranium billet removed. Billets of excellent quality can be produced by this process but unless the calcium fluoride lining is kept clean and dry, the uranium tetrafluoride free from oxyfluoride, and the reacting materials free from air the billet is contaminated with a considerable amount of slag and oxide. The billets produced are not, therefore, usually of sufficiently high quality to permit direct working of the metal without an intermediate casting process. Melting and casting is, however, desirable because it is the most convenient method of removing hydrogen derived from moisture in the reactor materials.

More recently magnesium reduction, which offers a considerable economic advantage because of the lower cost and higher purity, of magnesium compared with calcium has been introduced. This method has, however, the disadvantage that the heat of reaction of uranium fluoride with magnesium is much lower than with calcium so that production of a suitable solid billet requires greater care. In addition the higher vapour pressure of magnesium compared with calcium

would result in considerable losses by evaporation and cause oxidation and spongyness due to turbulence.

These difficulties have been overcome by carrying out the reaction in a bomb under low pressure. Many of the difficulties associated with mould lining for calcium reduction may be overcome by employing a reusable graphite lining. The magnesium is used in the form of turnings and the reacting material is mixed in the same way as in calcium reduction. Alternatively prepelletting may be employed to produce a more uniform reaction. An excess of magnesium is used depending on the size of the reduction. In British practice ingots of roughly 300 lbs. weight are produced by calcium and up to 500 lbs. by magnesium reduction. Magnesium reduced billets would have been quite satisfactory for direct fabrication by mechanical working, but since in fact practically all British fuel elements are produced by direct casting, direct mechanical working has so far been carried out on an experimental scale only.

Fabrication Methods

Almost every possible fabrication technique has been examined by British metallurgists and in some cases considerable quantities of fuel elements made. These techniques have included rolling, extrusion, push-bench drawing, cold drawing, various methods of tube and wire drawing, but experience has shown that casting is the most economic and satisfactory process for any fuel element for which it can be used. Where this is not practicable, as, for example, in the case of bars of length of 10 ft. or more, or where some special design feature is incorporated, such as, for example, a bonded-on can, rolling or extrusion methods have had to be employed and the fuel elements so produced have proved satisfactory.

Casting : Two basic types of casting furnaces are in general use for uranium, high frequency induction melting and arc melting. The arc type (fig. 4) is of use generally for those comparatively highly alloyed materials which melt at a high temperature, react with the crucible or mould or where very special properties are required. It cannot be used for complicated shapes and the comparatively poor surface which is often produced may result in a considerable loss by machining from the casting.

Practically all the high purity uranium which has so far been used has been melted by high frequency. The crucible material used is electrode graphite. Alternative materials are the refractory oxides, urania, beryllia, zirconia, magnesia, etc. but these are expensive, brittle and difficult to fabricate. Common electrode graphite handles well and can be readily machined to crucibles and provided a temperature in the region of 1600°C is not exceeded carbon pickup does not exceed 400 parts per million and the crucibles can readily be cleaned and reused several times. Surprisingly enough uranium metal can be melted in

air in a graphite crucible but this is wasteful and it is better to prevent surface oxidation by protecting the melt.

The first castings in Great Britain were made from a conventional high frequency furnace, holding about 400 lbs. of uranium. Oxidation of the uranium was prevented by the use of a flux cover of barium chloride. The metal was bottom poured by means of a stopper which consisted of a pointed bar, held in the hole in the bottom of the crucible by a strong spring. The bar was raised by means of a handle and the uranium ran direct into the mould below. This method produced perfectly satisfactory castings, but was abandoned because of the difficulty of obtaining sound graphite crucibles. When a porous crucible was used the barium chloride which had considerably greater wetting power than the uranium ran down the wall of the crucible into the mould. The castings so produced consisted of a mixture of barium chloride and uranium which was far from satisfactory.

For this reason methods of vacuum casting which were highly successful and have been used ever since have been developed. A furnace of this type is shown in fig. 5. It consists essentially of a water cooled bottom chamber, evacuated through a large diameter pipe, and a top assembly consisting of a silica tube round which is placed the induction coil. The top end of the silica tube is closed with a water cooled steel plate, the bottom end sits on a water cooled steel ring. All vacuum joints are made with rubber rings, greased with vacuum grease and where necessary compressed air cooled. The seal between the water cooled ring and the lower water cooled chamber is the only one which is broken in use. The top half of the assembly which is termed the furnace bell is lowered on to this by means of guides.

The connections to the coil, which is a water cooled copper tube, consist of busbars; these are bolted to main bushars after the furnace bell is lowered into position.

The inner casting assembly is mounted on the base of the main chamber. It consists of a crucible in which is placed the furnace charge, a launder system and moulds. As in the case of the air melt furnace the pouring hole is in the crucible base and is sealed during melting by a graphite or alumina bung which is laid in position in the crucible. After the charge has melted and has obtained a satisfactory super heat, as indicated by the thermocouple in the furnace wall, the bung is removed by means of a graphite rod, a system of bell cranks, push rods and lever which communicates to the outside of the case. The uranium metal then runs through the pouring hole in the crucible, down the launder and into the mould below.

After casting, the seal between the lower launder and the ring is broken, the bell raised and the crucible and mould assembly removed from the furnace and dismantled elsewhere in the foundry. An alternative type of furnace which has also proved highly successful has

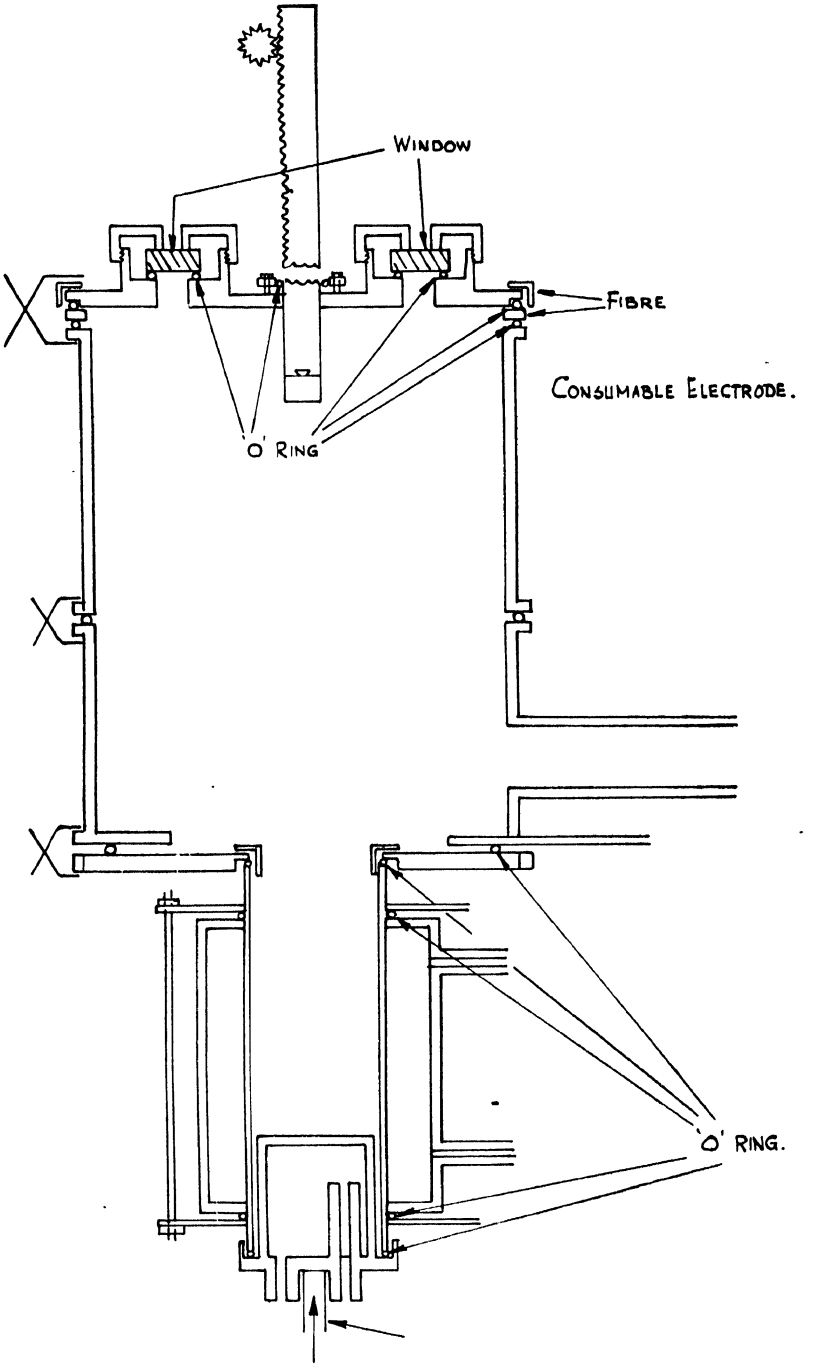


Fig. 4—Consumable electrode vacuum arc melting furnace.

the coil as well as the rest of the furnace assembly mounted inside of the vacuum chamber. The heating of the steel container in this case is prevented by means of a special shielding device. The design of crucible, launder, etc. is fundamentally the same in both cases.

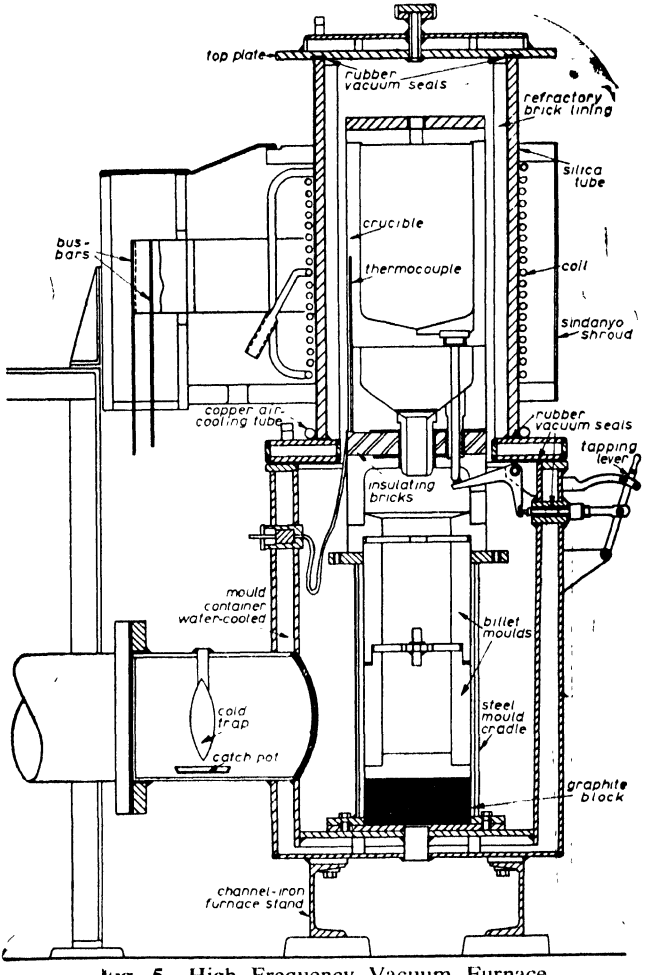


Fig. 5—High Frequency Vacuum Furnace

The process of melting refines to some extent; the oxide and fluoride present in the reduced metal float to the top and together with some of the oxide skin of the billet remain in the crucible. The hydrogen gas content which in the case of the billet is usually about 8 ppm is reduced to approximately 2 ppm by casting. Moisture in the oxide is removed during heating, and condenses on the cold trap in the vacuum connection. For normal uranium casting it is desirable to maintain a vacuum better than .5 millimeters of mercury. If necessary,

e.g. when melting very pure oxide free uranium, a vacuum of the order of 1/10th micron can be obtained by the use of a diffusion pump for most of the casting cycle, although gases evolved during melting and casting operations will temporarily raise the pressure (fig. 6). The mould material may be graphite or mild steel. A refractory dressing

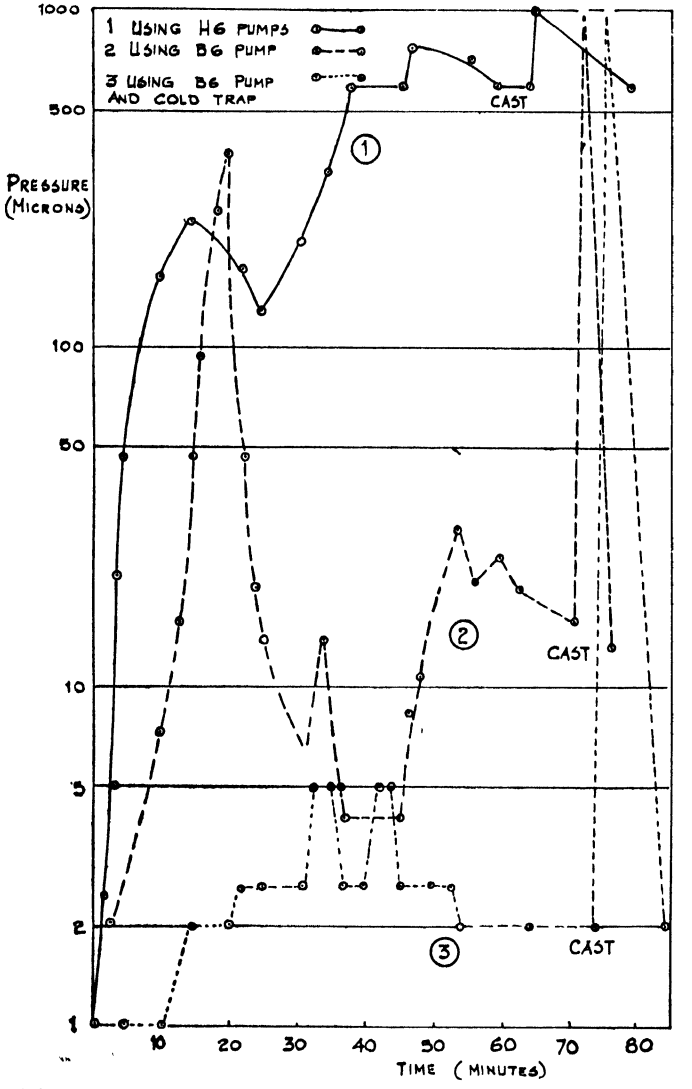


Fig. 6—Time pressure relationship of bar casting furnace. (AERG M|R 697)

is necessary to eliminate cold shots and inclusions and in the case of mild steel moulds prevent reaction between molten uranium and the mould. The most suitable material has been found to be alumina

which combines the properties of cheapness, thermal insulation, inertness to uranium at the pouring temperature and can be made moisture free by heating to a low temperature so that blow holes are not produced. The high specific gravity of uranium assists feeding the castings and if top running is used less header metal is required than for most metals. Advantage can be taken of this for the manufacture of simple castings of small dimensions. For example, moulds for casting bars of approximately 1" diameter can be designed so that the metal flows into them at a rate that keeps pace with solidification, so that the metal feeds itself as it solidifies and large additional feeders are not required. To some extent large castings can be made on this principle also; for example, the top of a large rolling billet can be arranged to be in the field of the induction coil so that the mould gets hot at the top. This results in very efficient feeding and only a very small sized head is required.

Careful choice of mould dressing and a proper design of mould can result in castings being produced to a high finish at very small tolerances; thus, bars or tubes can be precision cast within ± 0.004" per inch diameter. This tolerance is satisfactory for a great many requirements. Where dimensional accuracy demands that the casting surface be machined, the machining allowance can be kept very low. This is made possible by the absence of a gas which might be entrained by turbulence and by the mould dressing whose thickness can be controlled to eliminate cold shuts.

Vacuum casting has been developed to very high perfection and is extra-ordinarily versatile. Cylindrical bars up to 6 ft. long and $\frac{1}{2}$ in. diameter have been produced. Castings weighing a quarter of a ton have been made with some faces left as cast. To the other extreme castings with ruling sections of a 20th of an inch have been produced in some cases many thousands at a time. The scale of operations includes furnaces taking as much as one ton of uranium while at the other extreme vacuum furnaces containing about 2 lbs. are in use.

Most of the fuel elements used in England have been cylindrical bars roughly 1" diameter and varying from 1 ft. to 4 ft. in length. In some cases however bars of 8 ft. to 10 ft. in length have been required for export to countries operating other types of reactor. Were casting used this would necessitate the joining of bars by mechanical methods or welding. Welding methods have in fact been devised for uranium (fig. 7) but the lack of knowledge on the irradiation behaviour of the welds have so far precluded their use. Therefore in the manufacture of such elements a technique of rolling has been used.

Working : Before considering such methods of production, it is however desirable to consider the deformation characteristics of uranium. Uranium metal exists in three allotropic modifications, alpha, beta and gamma. The alpha phase which exists at temperatures up to 660°C has a hardness of about 200 brinell and is comparatively

brittle at room temperature. This hardness decreases with increase of temperature to about 30 brinell at 650°C. The beta phase (660-750°C) is hard and brittle and mechanical working in this phase is not considered. The gamma phase which exists between about 750°C and the melting point is cubic, very ductile, and soft. Pure uranium can therefore be fabricated readily by rolling at temperatures between 500-650°C and by extrusion at temperatures above 750°C.

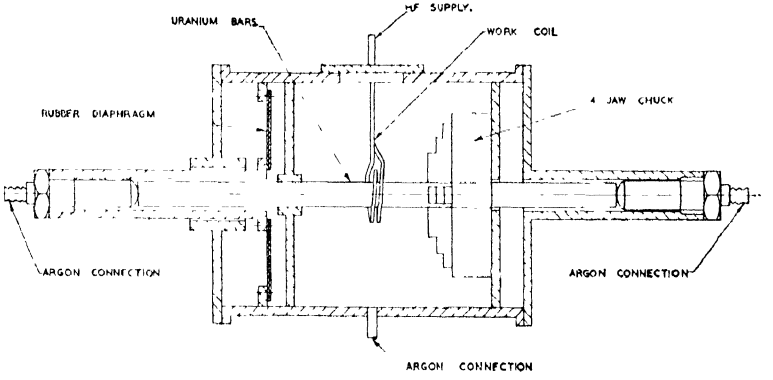


Fig. 7—Chamber developed for the pressure welding of uranium bars.

The most convenient method of expressing deformability in mechanical working is by means of the extrusion constant. Variations of this with temperature is shown in fig. 8. Alpha uranium is highly anisotropic and the temperature of working has an important effect on the structure, giving different degrees of preferred orientation which have a marked influence on irradiation behaviour.

In order to prevent the reaction of uranium with air it must be protected during heating before mechanical working. There are two basic methods of doing this, either the use of an argon or vacuum atmosphere in the furnace or by the use of a salt bath.

A convenient temperature range for rolling uranium is between 400° and 600°C. Below 400°C uranium cold-works rapidly and though thin material in sheet form can be given cold reductions of 80% before cracking occurs, large section bar or sheet may be deformed to a very much smaller extent. In the beta phase above 660°C uranium is much more brittle and attempts to roll material of random orientation result in disintegration. If, however, material which has previously been rolled in the high alpha is allowed to rise in temperature until it enters the betaphase it rolls readily. Above 770°C uranium rolls easily, but the material is so soft that bars in this temperature range are very difficult to handle, owing to their density and very low resistance to deformation.

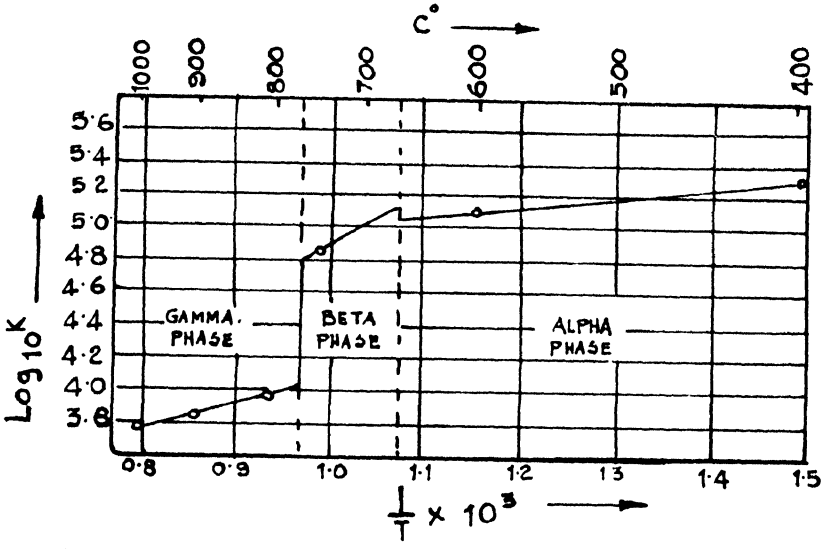


Fig. 8—The variation of the extrusion constant of uranium with temperature.

Material rolled at high speed in the alpha phase heats rapidly during rolling due to friction, both internal and between rolls and stocks, caused by the large force required to accelerate this high density material. If temperature control is not important this eliminates reheating, but if a controlled as-rolled structure is required it is essential to return to the heating furnace, which in this case is most conveniently a salt bath, in order to maintain a constant temperature. Round rolls of the type shown have several advantages. In the first place roll contact with the greater part of the surface of the bar results in the compaction of the oxide skin, and greatly reduces the amount of oxidation. Round rolls are also superior to those of the Gothic or oval type in that the majority of the uranium bar is under compression, and therefore less likely to crack than when an appreciable amount is free from the rolls and therefore under tension only. Round rolls are not at such a disadvantage for rolling uranium as they would be for some metals, because it is necessary to avoid the very large reductions used in Gothic or oval passes which cause overheating. In some cases it is desirable to hold the temperature of rolling very close and for some purposes this can be judged by eye. When more accurate control is required, however, it is desirable to mount a salt bath in close proximity to the rolls and replace the bars in this for heating or cooling as necessary.

Extrusion has only been used to a small extent for the manufacture of experimental fuel elements. Extrusion in the gamma phase presents a considerable die problem because the metal alloys rapidly with the metals of the iron, nickel and cobalt group at 735°C and if extru-

sion is carried out at temperatures greater than this precautions have to be taken to avoid contact.

When extrusion is used for the manufacture of a fuel element having a bonded-on zirconium can this is not a serious disadvantage as the zirconium which itself is usually canned in some material like copper, helps to separate uranium and die. For bare extrusion, hard metal dies of tungsten or titanium carbide are satisfactory though expensive and brittle and their life in an extrusion shop is not high. Stellite has been used with some success both for the die and as a coating for container and ram. Little alloying difficulty is experienced between stellite and uranium because the stellite is so hard that the oxide film of the uranium prevents true metal to metal contact. When extruding tube the die problem is even more serious as attack on the mandrel is very considerable. Stellite and carbide mandrels have again been used satisfactorily but are even more subject to breakage than dies.

The method of alpha phase extrusion of uranium which has been used in America has found no application in England as although the die problem is greatly eased the high pressures required are too much for most presses. Whether alpha or gamma extrusion is used the bar must be protected from oxidation. This is achieved by using an argon filled container coupled to the die, the argon also helping to protect the billet and container before extrusion.

Performance of Uranium under Irradiation

Uranium Growth : It seldom happens that uranium as fabricated is in suitable form for irradation as a fuel element. The reasons for this are best understood by consideration of the behaviour on irradiation of a hypothetical single uranium crystal. Alpha uraium has an orthorombic structure which can be described with reference to three crystallographic axes at right angles, [100], [010] and [001] (fig. 9). Upon irradiation at up to 400°C this crystal changes markedly in shape. It increases in length in the [010] direction, decreases correspondingly in the [100] direction and does not change in the [001] direction. This dimensional change is temperature dependent. It reaches a maximum at about 200°C where the length of a single crystal roughly doubles for 0.1% burnup and decreases progressively with temperature until it dies away exponentially at about 400°C. If, therefore, a fabricated component has a large grain size, those crystals with their <010> axes perpendicular to the surface will tend to stick out on irradiation and those with their <100> axes perpendicular to the surface will tend to sink down with considerable roughening of the surface. Such a surface is shown in fig. 10. The roughening will decrease as the grain size decreases and will cease to be evident if the grain size is small enough. In either case if the structure is random (an equal proportion of each of the three axes lies in any direction) no overall change in dimensions will occur, but if there is a preferred orientation in any direction, the component will elongate in that direction containing the

highest proportion of <010> and shorten in that direction containing the highest proportion of <100>.

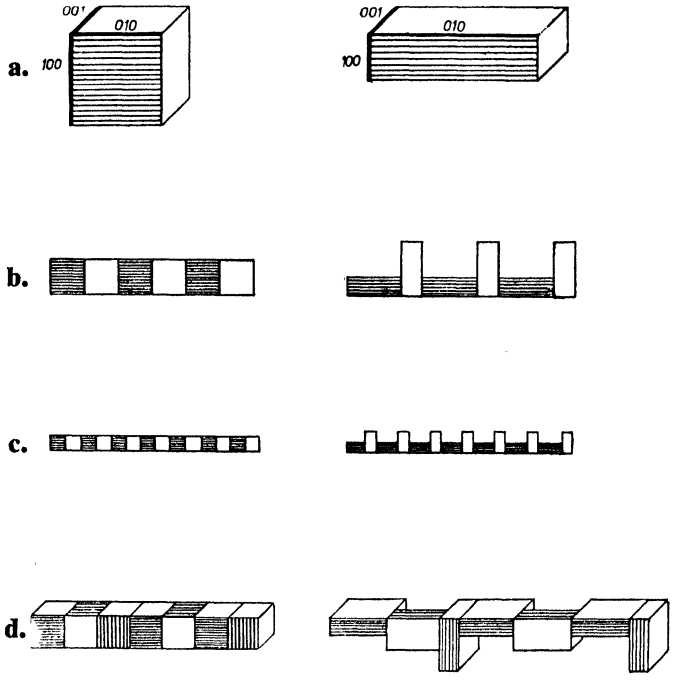


Fig. 9—Uranium before (left) and after irradiation (right)

a. A single crystal of uranium after neutron bombardment increases its 010 direction, shortens in the 100 direction, and remains unchanged in the 001 direction.
b. A coarse-grained random structure becomes increasingly wrinkled.
c. A fine random structure remains comparatively smooth and stable.
d. A structure with a high 010-preferred orientation increases in length. These are always fine grained.

For dimensional stability up to 400°C, which includes the operating temperature of most of the early reactors based on uranium metal it is essential to have a fine random grain size.

Similar effects to those described for irradiation can also be produced by cycling uranium between two temperatures. The uranium crystal shows a high degree of anisotropy in its thermal expansion which has the approximate values 25 x 10^{-6} in the [100] direction, -3 x 10^{-6} in the [010] direction and 24 x 10^{-6} in the [001]. When, therefore, two adjacent crystals are heated they impose mutual stresses at the junction. If the [010] axis lies in the plane of the two crystals parallel to the [100] axis in the other the first crystal will be stressed in tension on heating and the second crystal in compression. The resistance of the crystals and the crystal boundary itself to stress varies with temperature and the crystal which resists strain in the high temperature in one direction may

be weaker at the low temperature in the other. In addition grain boundaries are relatively weaker at the higher temperature. In a random structure these strains cancel out except at the surface which wrinkles in precisely the same manner as similar specimens under irradiation, depending on whether the grain size is large or small. When preferred orientation is present the component may elongate or shorten and this may be in a direction in which there is a preponderance of large thermal expansion differences or alternatively it may be in the direction in which the grains are longest. For all practical purposes both these mechanisms operate to cause elongation in the direction of working in a material in the alpha phase and this may or may not concide with the change of shape due to irradiation. The desirable structure for stability under both irradiation and thermal cycling is a fine grain with random orientation.

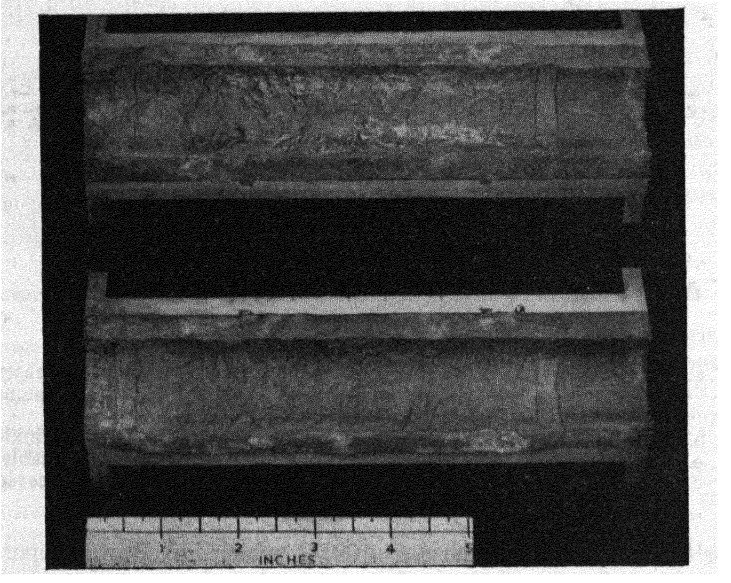


Fig. 10—Wrinkles on an irradiated cast Uranium bar are reproduced by pressing on to lead.

Cottrell Effect : The shape changes undergone by uranium under irradiation can have a significant effect on the mechanical properties of a polycrystal. Under creep conditions the mutual impingements of differently oriented grains will prevent the material opposing its full yield strength to the applied stress.

The variously oriented growth strain will reach the yield point in a time :

$$t_m \simeq \sigma_y / E\epsilon'_g$$

where σy and E are the appropriate yield strengths and elastic constants, and ϵg is the rate of growth. (For a neutron flux of $10^{12}cm^{-12}$ sec^{-1} at 200°C ϵg is approximately 4 x 10^{-9} sec^{-1}).

If after time t_m a stress σ is applied an overall elastic deformation σ/E occurs.

In addition an overall plastic deformation of order σ/E also occurs due to the overall plastic relaxations under the combined influence of the internal and applied stresses. These relaxations must be neutralised before the overall plastic deformation can continue, and this will take a time of the order of t_m. Hence during each interval t_m an increment σ/E of overall plastic deformation takes place so that if ϵe is the strain rate under the applied stress

$$\epsilon e \sim \left(\frac{\sigma}{E} (\sigma/\sigma_y)^{\epsilon} g \right)$$

which gives a creep rate of $10^{-10}sec^{-1}$ under an applied stress of 1000 p.s.i. at 200°C. (This rate of strain is linearly related to stress). There would of course be no creep under these conditions in the absence of irradiation.

The existence of the phenomenon (now known as the Cottrell effect) was demonstrated by measuring the deformation of an axially loaded spring of uranium. Fig. 11 shows the behaviour of such a spring. The agreement between prediction and experiment is surprisingly good.

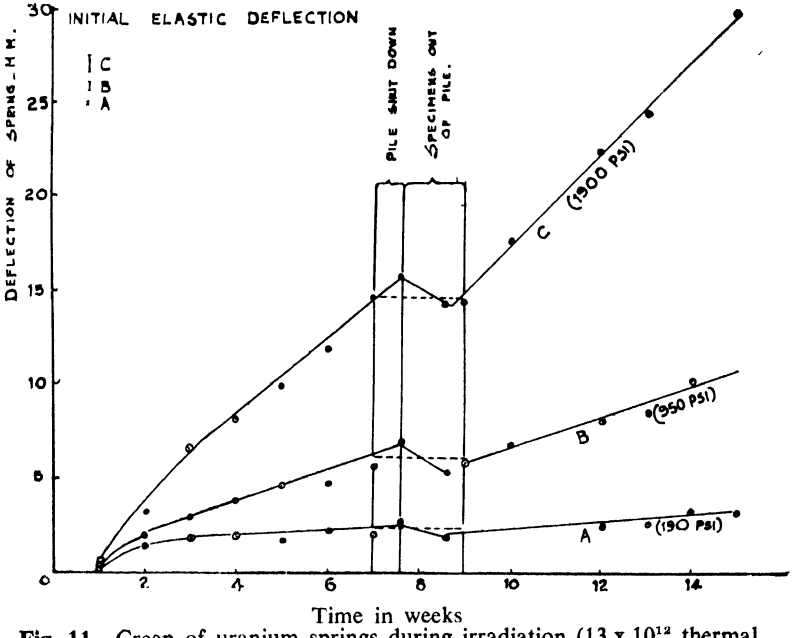


Fig. 11—Creep of uranium springs during irradiation (13 x 10^{12} thermal neutrons per sq. cm. per sec.) at 100°C. The stress valves refer to mean skin stresses.

The importance of the Cottrell effect in reactor design may be illustrated by considering each stacked fuel element in the first charge of the Calder Hall reactor as an axially loaded strut. (Fig. 12).

Any departure from straightness (or any non axial load) will cause a bending stress on the element which will lead to an increase in bow, and therefore an increase in bending stress.

The time taken for a given bow to double itself is given by the relation :

$$t_D = 0.693\ TI^2\ EI/(P+0.6\ W)L^2$$

where P is the end load, W its weight, L its length, I its section modulus, and E is a parameter stress/strain rate determined for the material, temperature and irradiation rate by measuring the rate of sagging of a horizontal bar supported at each end. For Calder conditions the rate of bow is such as to cause the fuel element to impinge against the side of the channel after a few hundred megawatt days per tonne, with a serious risk of jamming.

Methods of measuring fuel element bow (by radiographing the fuel element adjacent to a straight edge) were devised which indicated that the predicted deformations were of the right order, and led to an early discharge without troubles due to jamming.

For the second and subsequent charges support braces taking the form of longitudinal Magnox skates or splitters fixed on the outside of the fins were devised. If the fuel element bends these butt up against the side of the channel and prevent further distortion.

A rigid central brace effectively halves the length of the fuel element and might be expected to increase the resistance to bowing by a factor 4. Long braces produce much greater improvements.

Swelling : At high temperatures and irradiations the most serious problem presented by uranium under irradiation is fission product swelling. The uranium atom fissions into two atoms of lesser atomic weight and a number of smaller particles. These lighter atomic weight elements have larger atomic volumes than the uranium they replace and cause an increase in the volume of the material by some 2 to 3 percent per percent of uranium fissioned, which is not a very serious matter. Roughly 10% of the fission products, however, are permanent isotopes of the noble gases Krypton and Xenon and for every 1% of uranium atoms fissioned roughly 4.6 ccs of gas at N.T.P. are produced per cc original uranium. It has been shown that these atoms can diffuse in uranium and can be desorbed from its surface but cannot be re-absorbed.

These atoms congregate in colonies, formed on flaws, discontinuities or arising in other ways, which form gas pockets, and later bubbles, and cause large increases in volume and later disruption (Fig. 13).

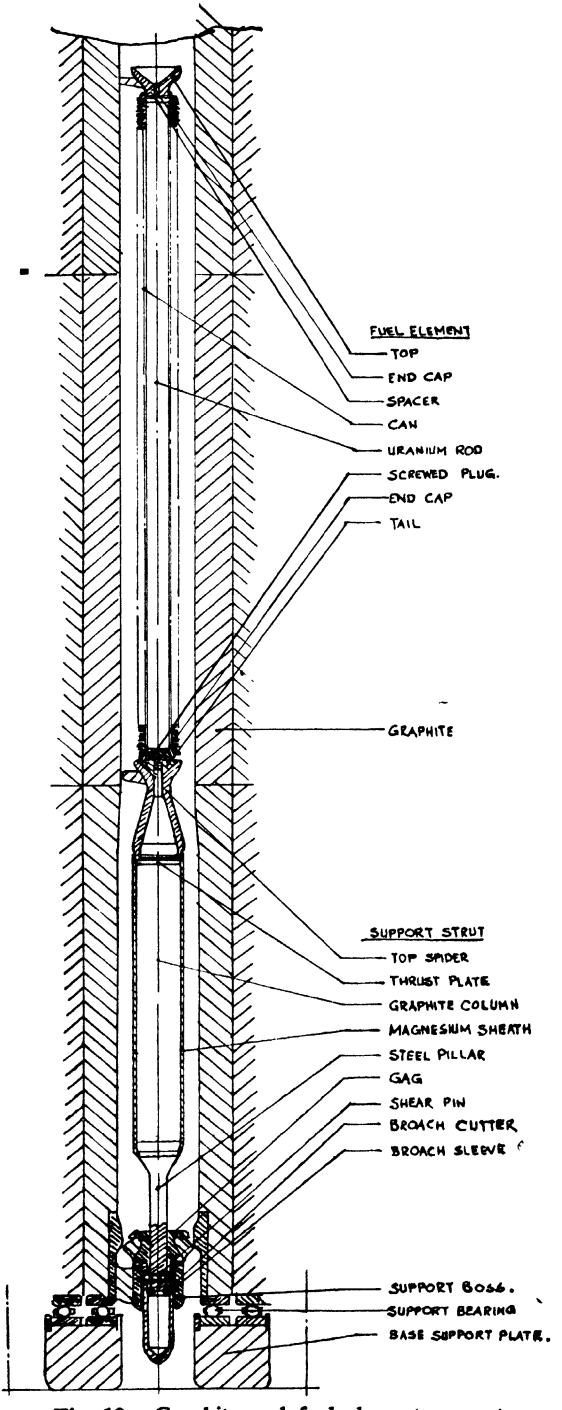


Fig. 12.—Graphite and fuel element support.

These increases in volume may be calculated given a knowledge of the creep strength of the uranium, but so far the calculations give low values compared with those observed. The highvalues are probably caused by anisotropy, phase transformations and fission effectively reducing the creep strength. They may be overcome by the use of isotropic, single phase high creep strength materials such as the 14% molybdenum alloys, but such alloying adversely affects neutron economy in thermal reactors.

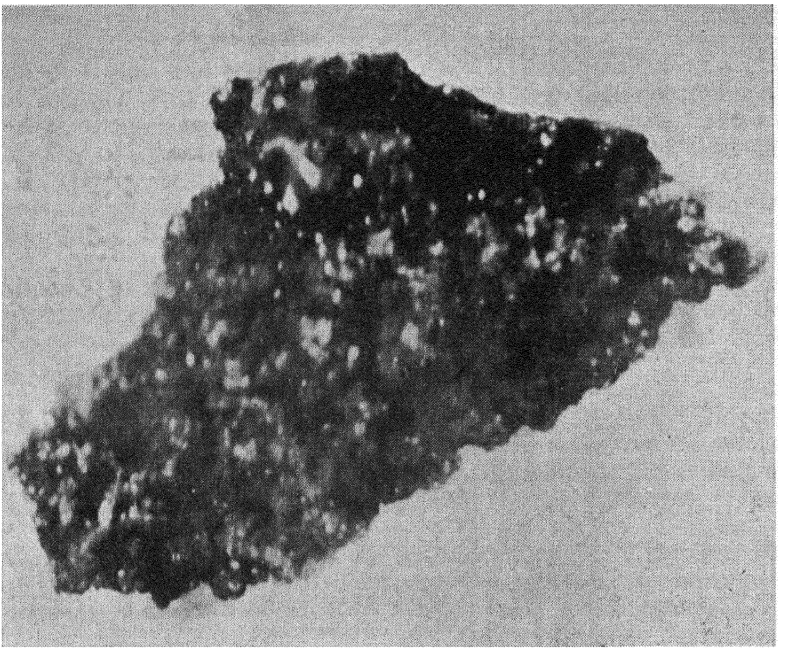


Fig. 13—Disruption of uranium by fission product gas at high burnup.

Uranium Structure

There are two important types of structures of uranium metal—those which arise as a result of the transformation from beta to alpha and those which arise as a result of mechanical working, generally followed by annealing. The most important class of structure is that produced by cooling through the transformation and these include those produced directly by casting and also those arising by what is known as beta treatment. The cooling of uranium through the alpha beta transformation and the structures so produced are governed by laws which can be expressed as time, temperature transformation diagrams in a similar way to that of steel and the subject is best approached by considering a typical diagram, that for uranium 0.3 at % chromium alloy

as shown in fig. 14. The most interesting feature in this diagram is the existence of 2 C_S which indicate that there are two transformation mechanisms, one at high and one at lower temperatures. These two mechanisms are entirely different in nature; the higher temperature mechanism consisting of nucleation and growth phenomena occurring within the crystal while the lower temperature transformation is martensitic or shear type. With very low alloys the curve is shifted far to the left and only the martensitic transformation operates. With high alloys, particularly of chromium the curve is shifted to the right, only the upper nucleation and growth transformation is operative and the beta phase can be retained for comparatively long periods.

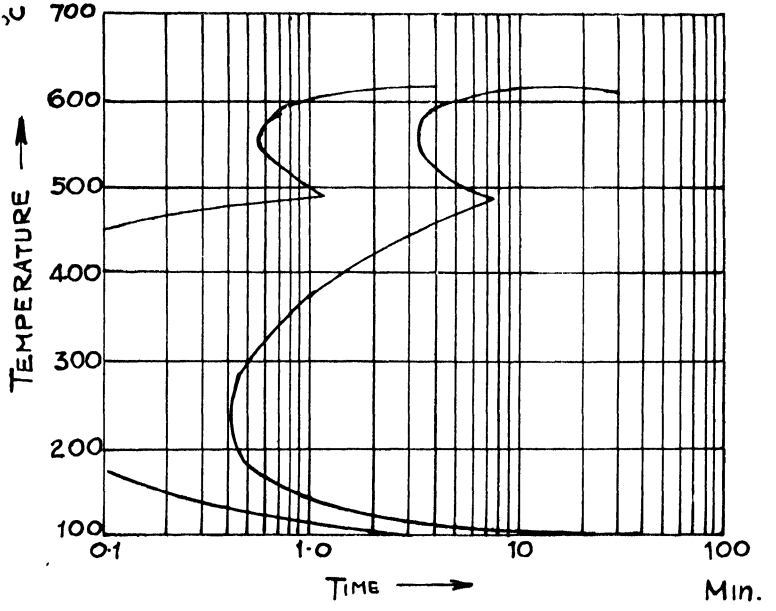


Fig. 14—TTT curve for uranium. 0.3 at % Chromum Alloy.

The exact mechanism of transformation is still under discussion but the results are basically this. Uranium heated from the alpha to the beta phase undergoes a randomizing action because each uranium crystal can transform in any one of 24 different directions and this number can be increased, if as generally happens twins exist in the alpha uranium crystal, thus whatever the original structure uranium which has been heated and cooled once or twice through the transformation is effectively random. If a low alloy material is quenched so that transformation on the lower 'C' occurs at a low temperature, nuclei start from a great many points from the crystal, grain growth is comparatively slow and a fine random grain structure results.

If, however, the crystal is slowly cooled nucleation only occurs at a few points. The rate of propagation is rapid and a generally large

crystal structure results. An important and perhaps somewhat confusing feature of this type of structure is the existence of sub grains in the large macro grains. Looked at by macro methods the grains can be ¼″ or more across and metallurgically and physically they behave as though they were such large grains. Careful investigation however shows that each grain is composed of a series of sub grains differing in orientation from each other only by a few degrees. Since the difference in orientation across the grain boundary of a macro grain may only be of this order grains appear to change in position according to the angle of the incident light. Such material strongly exhibits the phenomenon of wrinkling under irradiation. Grain refinement of highly alloyed uranium by quenching in water is not possible because the material tends to crack under this treatment. It is necessary therefore to carry out an isothermal treatment that is to quench into a salt or metal bath at a temperature at which a fine grain is produced by the nucleation and growth mechanism. Fine grained random structures can be produced very consistently in this way but the process is more complicated and expensive than water quenching and requires more alloying material which may adversely affect the neutron economy of the reactors.

The other family of structures produced are those produced by uranium working in the alpha phase. Uranium worked at low temperatures in the alpha phase deforms by a twin mechanism and the resulting cold worked heavily twinned structure has a strong preferred orientation in the [010] direction. As the temperature of working increases a slip mechanism takes over and becomes dominant in the very high alpha, this results in the appearance of a [110] texture, the proportion of which increases from about 400°C upwards until it is the major texture at 630°C. At intermediate temperatures mixed structures are produced, some of which have considerable importance technologically. These worked structures are always of a fine grain size.

Annealing of worked structures follows much the same rule as those which come from the annealing of normal commercial metals. Twinning or work hardening are removed or reduced. Fine grain structures free from sub grains are formed and orientation is only affected slightly there being perhaps a slightly higher tendency to form [010] in annealed structures than in as-worked structures. Working can also be carried out in the beta and gamma phases. Gamma worked structures obey the same rules when cooling through the $\gamma \rightarrow \beta$ phase transformation as cast material and the effect on the properties is very similar. Material worked in the β phase is usually fine grained random in structure but the difficulties of control make this an unsuitable method of production.

Two basic techniques are available for the production of the desirable quenched structures, high frequency induction and salt bath quenching. The salt bath method was developed first; this consists of

immersing the component in a bath of mixed salts or metal which has been chosen carefully so that it does not attack the uranium. Chloride or carbonate baths are normally used. The bar is then removed and inserted in a bath of water or another salt at a lower temperature according as to whether beta quenching or isothermal treatment is required. Provided care is taken to provide uniform heating and to carry out the quenching uniformly so that no bending stresses are produced, this method produces very satisfactory results but is messy.

Induction heating is much more elegant. Single shot or traverse quenching may be used. For single shot quenching the bar is held or suspended in a large induction coil and the whole length heated simultaneously, after which it can either be removed and dropped in the necessary water or flux bath or water can be introduced into the rig. Alternatively the method of traverse quenching can be used, this passes the bar downwards through a heating coil beneath which is a water spray and further down still a tank of water. This is by far the most elegant process but needs very strict control to maintain uniformity of grain structure, freedom from bending and overheating at the ends of the specimen. The method has however been employed very successfully and is extremely suitable for production.

Fuel Elements

Bepo : Four kinds of uranium metal fuel element have been developed in Britain. The first type were the finned aluminium "cartridges" used in BEPO and the Windscale Piles, which were very

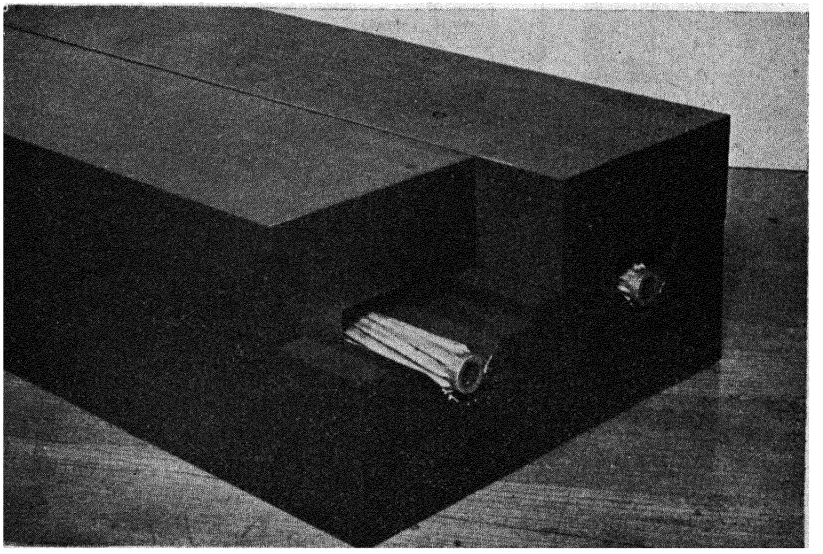


Fig. 15—Bepo Fuel Element in Channel.

similar in principle. The second were the long canned aluminium bars used in the NRX and the Halden Reactor. The third the magnesium canned fuel elements for Calder Hall and the industrial power reactors, and the fourth the high temperature elements for the Dounreay fast reactor.

The BEPO fuel element, is a finned canned uranium rod, 0.9″ dia by 1′ long which lies horizontally in a V shaped trough running through the pile. Charging and discharging are carried out by pushing the string of elements through the pile, and the ends must be designed to accommodate this.

The rods are made by casting, in some cases followed by machining, but in other the as cast surface was used. Early elements contained rods in the as-cast condition but later ones were heat treated, at first by salt bath quenching and later by high frequency traverse quench. A helium reservoir is machined in one end of the bar. The can is aluminium tube 0.025″ in wall thickness with fins roughly 0.125″ high and .015″ thick. It is made by impact extrusion from a hollow slug machined from a solid extruded tube (see fig. 16). The fins can be extruded helical by the use of a skew die, but it is impossible to guarantee the twist, and in most cases they are twisted on a lathe after annealing.

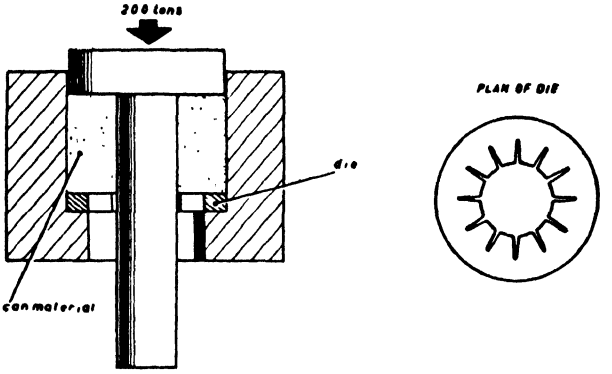


Fig. 16—Bepo type finned cans are made by impact extrusion. The Helical Twist in the fins is usually done later in a lathe.

End sealing is carried out by a combination of wealding, crimping and brazing (see fig. 17). One end of the can is sealed first, an anti diffusion barrier placed on the surface both of the can and bar to prevent reaction between uranium and aluminium to form UAl_2 at reactor temperatures (an oxide coat is effective), the bar inserted in the can, vacuum degassed to remove any volatile matter, helium filled, and the second end then closed in a similar way to the first. Present practice is to ensure a good fit between can and bar by "pressurising" in a hydraulic chamber. Considerable attention has to be paid to testing for weld tightness, and freedom from can/fuel diffusion.

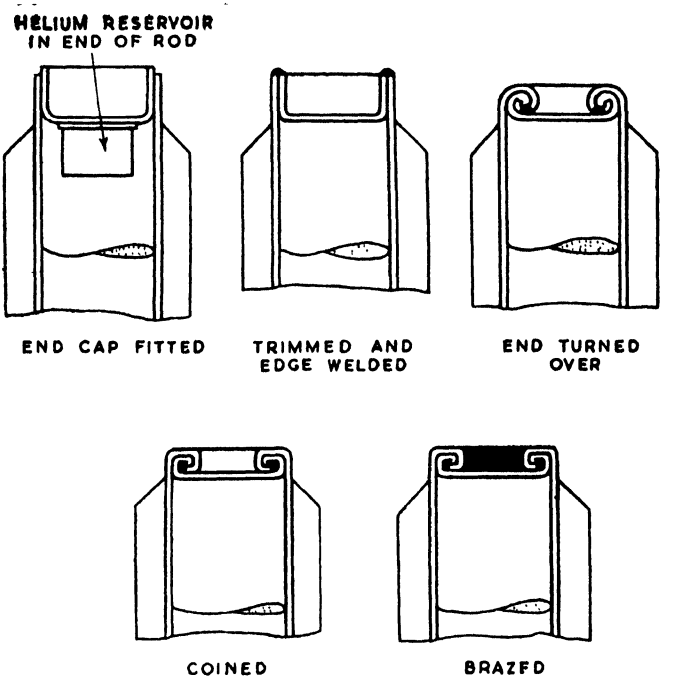


Fig. 17—Method of sealing uranium fuel containers.

Large holes in the seal are detected by heating in high pressure water at 150°C for periods of about a day, and small holes by detecting helium leaking out of the can into an evacuated chamber connected to a mass spectrograph.

The presence of helium in the can may be checked by measuring the conductivity of the bar/can gap by a calorimeter method. A low heat conductivity denotes the absence of helium.

Continuity of the anti diffusion barrier may be checked by heating to 350°C for a few days, followed by examination of the can surface for raised pimples or by radiography. (Fig. 18).

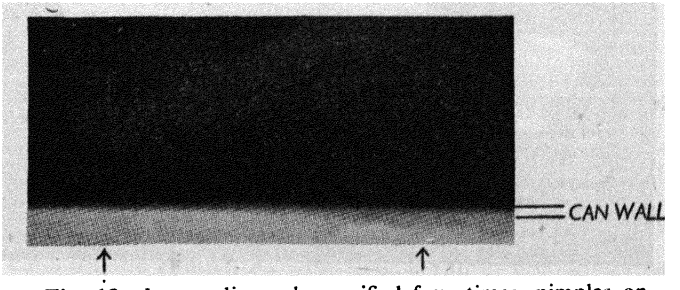


Fig. 18—In a radiograph manified four times, pimples on an irradiated element indent the can wall.

These cans have given reasonable service, no failures having resulted from leaks or alloying. The weakness has been tendency to fail by ratchetting due to the differential thermal expansion between can and bar. (figs. 19, 20). The phenomenon, which can lead to disruption of the can by intermittent tensile stresses is aggravated by the frequency with which the pile is shut down—a feature of an experimental pile.

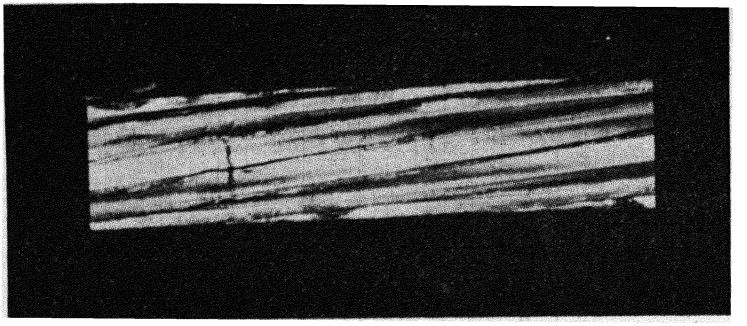


Fig. 19A

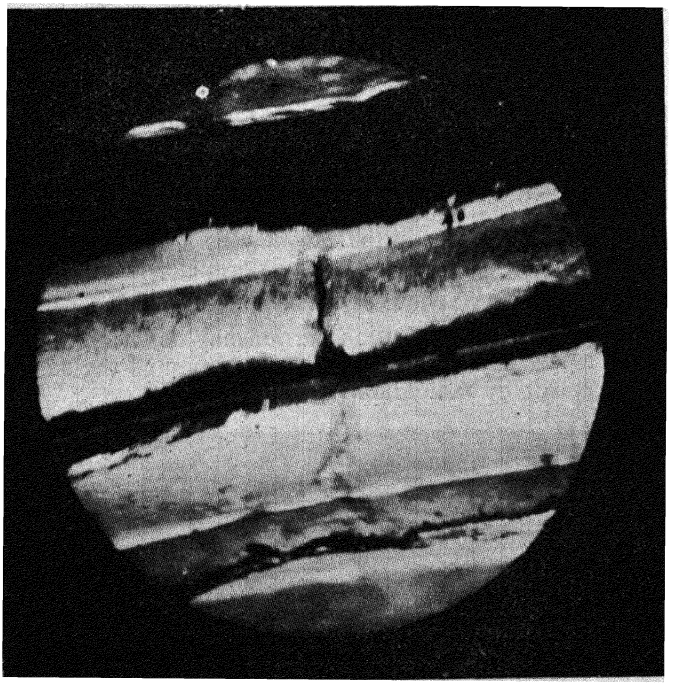


Fig 19B
Cracks in Bepo can be caused by ratchetting.

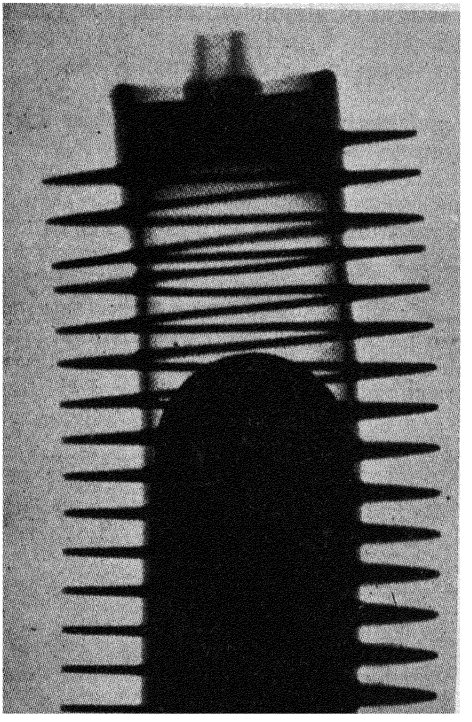


Fig 20.—Effect of ratchetting in experimental Calder Hall can.

In early fuel elements it was also aggravated by the tendency of the bars (which were not grain refined) to wrinkle, and by the fact that a very close fit had been achieved between can and bar by drawing on. The use of a much slacker fit, grain refinement of the bar, and the maintenance of a much higher helium pressure considerably alleviated the problem. Use of a higher strength can material (2 2% Mg, aluminium alloy) has had encouraging results but insufficient experience has yet been available on this technique.

NRX and Halden : Both NRX and the Norwegian Halden Reactor use long aluminium canned fuel elements. The uranium bars, of the order of 8 ft. long and an inch in diameter are rolled from vacuum cast ingot, straightened, heat treated by traverse quenching and machined.

The cans are of extruded aluminium. The American practice has been to port hole extrude hot, but techniques of cold so called impact extruding over a mandrel have been developed in England which can produce a "solid drawn" tube to close tolerances up to thirty feet long.

The cans for the Halden Reactor, which run at a comparatively high temperature are internally anodised by the sulphuric acid process to prevent alloying with the uranium.

The end pieces also of aluminium are screwed to the uranium rods, and sealed to the cans by argon arc welds. The testing programme includes heating in steam for several hours.

Calder Hall : The fuel elements for Calder Hall are of uranium metal 40″ long and 1.15″ dia. canned in magnesium based alloy. Uranium bars are heat treated, machined from cast uranium bars very slightly larger in size. The higher temperatures and pressures in Calder Hall compared with Windscale and BEPO would make can diffusion a much more serious problem than in the case of these piles and for this reason aluminium is impracticable. The material used is an alloy of magnesium with aluminium and beryllium, chosen on grounds of absence of can bar diffusion good weldability, resistance to oxidation by air, reasonable ductility and resistance to cavitation (to which magnesium alloys are subject under strain.) Fig. 21. All magnesium alloys

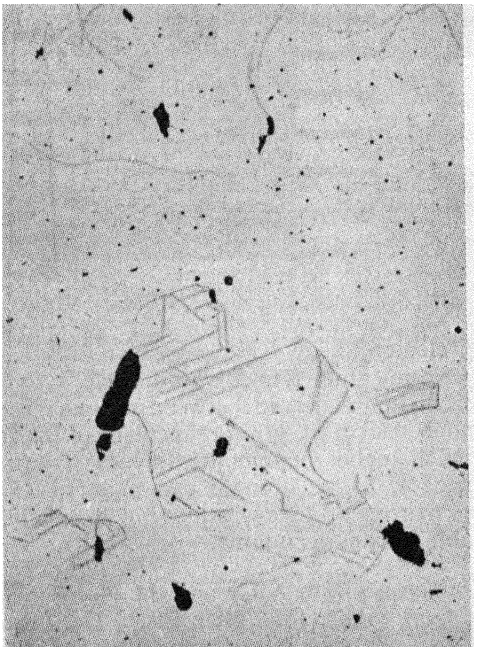


Fig. 21—Cavitation produced by creep strain in Magnesium Alloy.

are highly resistant to oxidation in CO_2 but the presence of beryllium is an additional safeguard and in the unlikely event of a failure of the coolant circuit, these alloys can be heated up to the melting point (and in some cases beyond) without serious oxidation occurring. Great care is taken during handling, cleaning and heat treatment of the uranium not to bend the bars in any way. The cans have so far been

machined from extruded bars, and have tranverse fins. They are sealed by inserting end caps and carrying out inert gas shielded edge welds. (Figs. 22, 23).

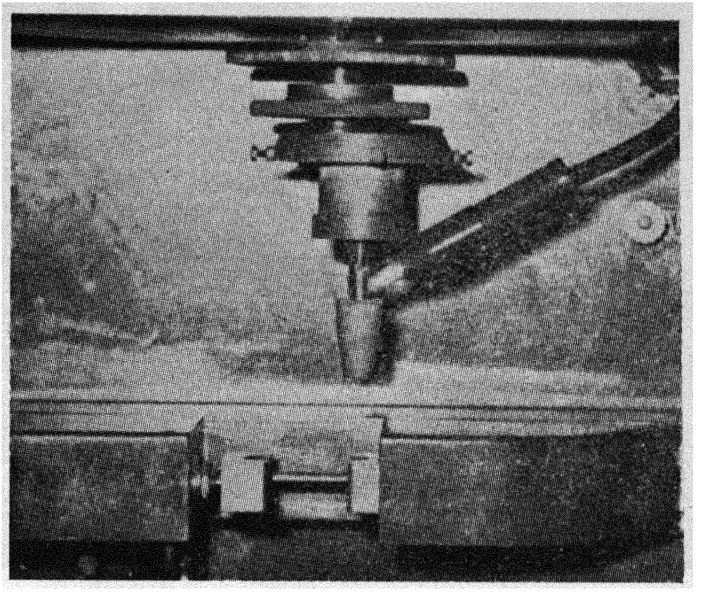


Fig. 22—Automatic Argon-Arc Welding equipment developed for assembling fuel can elements.

The cans contain helium at a low pressure. This is not added to facilitate heat transfer between bar and can because the hydrogen always present in uranium metal provides sufficient conductivity for that, but in order that the soundness of the cans and in particular the welds can be tested by a mass spectrograph method as described for BEPO.

Thermal ratchetting between can and bar is prevented by provision of evenly spaced grooves along the bar, on to which the can is pressurised as described for BEPO bars but at a somewhat elevated temperature. After manufacture but before testing for soundness the cans are cleaned to remove any uranium contamination on the surface which might interfere with the detection of bursts, by a process which can use citric acid with wetting agents assisted by mechanical brushing, this successfully removes all contamination.

The Calder fuel elements are stacked one above the other in a vertical channel, with cup and cone joints and support spiders at the end. The performance, so far as bowing is concerned has been described above (see "Cottrell Effect").

Irradiation growth and fission product swelling present no problems at Calder Hall temperatures and burnups.

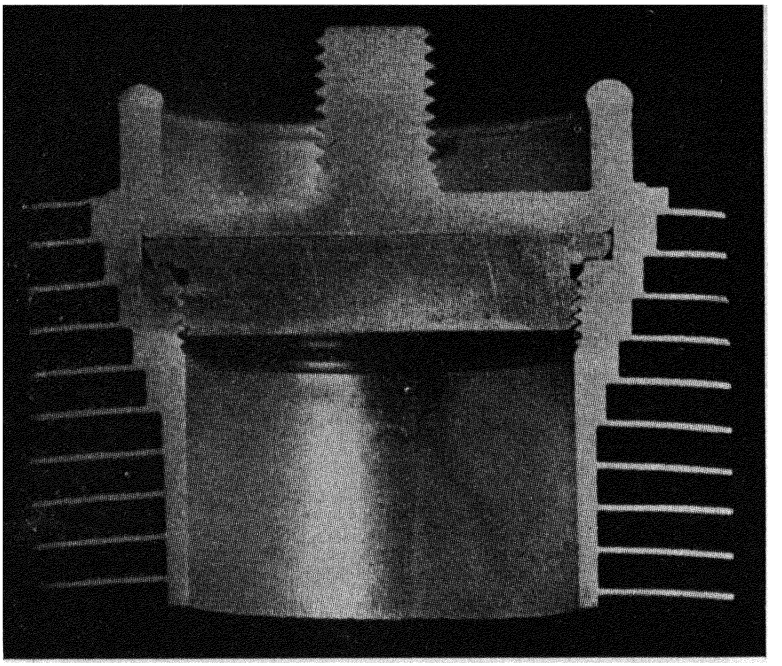


Fig. 23—Magnesium alloy fuel element with circumferential fins. These fuel elements have an edge-welded cap

During the comparatively short irradiation of the first charge however three fuel element defects were detected by the burst slug detection gear. Two of the elements were removed during shutdowns, specially scheduled for the purpose, and the third indication occurred near the already decided end of the life of the charge and was therefore left in until the whole charge was due for removal. The most satisfactory features of these incidents which were presumably due to tiny leaks was the slow rate of burst development which had been predicted from the characteristics of magnox and uranium and demonstrated in the early tests of sample cartridges with defects in them, heated in CO_2. In one case the defective fuel element occurred in one of the hottest elements of the reactor while this was running at considerably greater than design power. Although the fuel element stayed in for a fortnight after the burst was detected it proved extremely difficult either to locate the hole through which the carbon dioxide had penetrated the can or to find any effect of corrosion of the CO_2 on the uranium. In one case a small mound about a 10th high of oxide was observed and in the other cases even smaller mounds (Fig. 24). Even when the mound had grown and caused strain on the can wall only a slight cavitation of this can wall was noticed and there was no sign whatever of complete penetration. The two charges now in the reactor, the first charge of reactor No. 2 and the second charge of reactor No. 1 have been running for many

months somewhat above the design power, no sign of failure of any can has been observed and the braces are successfully restraining bowing. This speaks very highly for the basic design conception, the development work on materials and methods of fabrication and the actual manufacture of the fuel elements themselves.

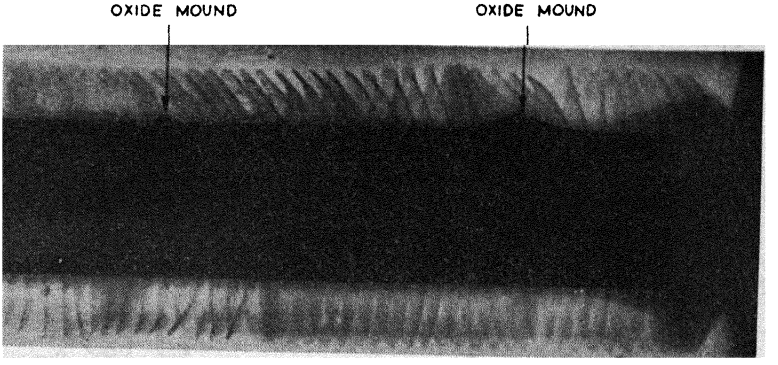


Fig. 24—Radiograph of Failed Calder Hall Cartridge.

Dounreay Fast Reactor : Fuel elements for the Dounreay fast reactor have so far been of an experimental nature only and no indications of their performance in a reactor will be available until some time next year. It is however possible to give some suggestions on the way such fuel elements could operate from a patent by Tottle and Kendall (Fig. 25) who were both concerned with the design of the reactor, which would seem to indicate that fuel elements could be a hollow tube about 4′ long of uranium metal canned in niobium on the outside and vanadium on the inside. The can is filled with sodium which is allowed to communicate with the coolant sodium through holes in the inner can which is in any case not welded to the end caps. Fission production expansion of the uranium is allowed for by leaving a dead space inside the can into which the uranium expands driving out the sodium. Dimensional stability of the fuel element is ensured by the hardness and strength of the canning materials which at the operating temperature are much stronger than uranium. In the design patent by Kendall and Tottle any rise in temperature causing melting of the uranium would cause failure of the inner can before the outer, the uranium would then run out down the hollow centre of the fuel element thus preventing any possibility of formation of a super critical mass by the whole of the uranium melting and solidifying in the lower part of the core. Great care has to be taken during the manufacture and fabrication of cans of the highly refractory metals such as niobium, or vanadium to prevent the absorption of oxygen during the production of powder, compaction, fabrication and annealing operations, as this can produce very brittle cans. Even more important is the maintenance of a low oxygen concentration in the sodium. All these metals are very resistant to pure sodium but the presence of slight traces of oxygen can cause pickup of

oxygen from the sodium to the niobium producing oxide on the surface which is rapidly removed by the following sodium and can erode the can.

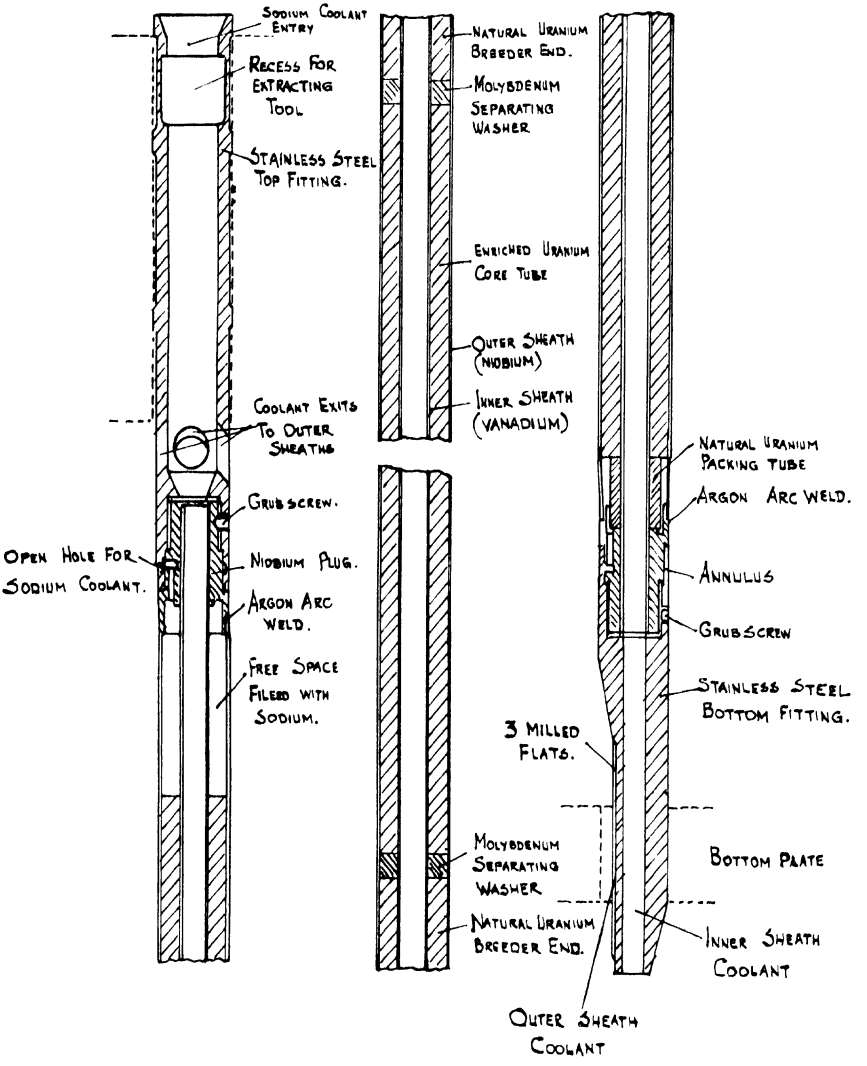


Fig. 25—The Dfr fuel element.

Acknowledgments

Most of the material for this lecture has been acquired as a result of the author's own experience. Use has been made of existing publicatios where they exist and more detailed information on some of the points raised can be obtained as follows :

"Production, Fabrication and Properties of Uranium-Progress in Nuclear Energy, Metallurgy and Fuels edited by Finniston and Howe, Pergamon 1956". Figs. 1-4, 6, 8 and 14 are included by permission of the publishers of this volume.

For more detailed information on fuel elements—"The Production of Reactor Fuel Elements"—by Wyatt. Nos. 1, 2 and 3 of Vol. 1 Nuclear Power.

For a full description of Calder Hall "The Journal of British Nuclear Energy Conference—Symposium Calder Works Nuclear Power Plant" from which figs. 12, 13, 20 and 21 were originally published in this volume.

A full account of the "Cottrell" Effect is given in "Creep of Alpha Uranium during Irradiation with Neutrons"—by Professor A. H. Cottrell and Mr. A. C. Roberts.

For further information on the welding of fuel elements materials—"Materials and Welding for Nuclear Power Fuel Elements—Vol. 25 No. 10"

The author wishes to express his thanks to Sir Leonard Owen, Managing Director of the Industrial Group, U.K.A.E.A. for permission to publish this lecture.

Fig. 23 is included by kind permission of Mr. G. B. Greenough of the Research & Development Branch, Industrial Group.

Discussions

Dr. D. P. Antia, (*Hony. Secretary, The Indian Institute of Metals*) : Can Mr. Wyatt give some further information on the following points :—

(1) strengthening of the aluminium can. Was it done by increasing the wall thickness or by use of some aluminium alloys.

(2) was there any special method used for anodising and if not what standard process was used.

(3) cans have been mentioned as having been made by *impact* extrusion. What was the maximum length of the cans made by such method.

Author's Reply : (1) The can was strengthened by the use of an alloy of aluminium containing approximately 2% magnesium.

(2) A method of anodising aluminium to prevent inter-diffusion has been described in "Canning for the Brookhaven Reactor"

by Gurinsky in the proceedings of the Geneva Conference. The method generally used is that of sulphuric acid anodising.

(3) Cans have been made upto 10 ft. long. The process should be described as cold extrusion rather than impact extrusion. With the hydraulic press used by Messrs: Accles & Pollock Limited of Oldling, Staffs England, a length of 30 ft. is theoretically possible, but whether in fact the lubricant used would be effective in such long lengths is somewhat doubtful.

Dr. K. Tangri, (*Atomic Energy Establishment, Bombay*) : I have noted with interest your remark that if material which has previously been rolled in the high alpha range is allowed to rise in temperature until it enters the beta phase, it rolls readily. As far as I know this observation has been made for the first time. A probable explanation for this perhaps would be that the texture developed during high alpha rolling results in a favourable disposition of the crystallites with respect to the mechanism of deformation of the beta phase. Therefore, it should be interesting and useful to study the crystallography of deformation mechanism in the beta phase. It may be that during the rolling process one might heat the metal slowly into the beta range and quench the rods as they come out of the rolls. This seems to be an interesting and economic proposal worth looking into. I would appreciate it if Mr. Wyatt would comment on it.

2. Mr. Wyatt has made a good case for the preference of round roll passes over gothic or oval. I would like to offer another supporting reason, in addition to the ones already mentioned by him. It is known that the radial distribution of (002) planes which lie parallel to the rod axis, is nearly symmetrical in a rod rolled with round passes, as contrasted to the highly asymmetrical pattern that results from the oval, edge-oval pass sequence. It is quite likely that the asymmetric nature of the probable residual texture after beta treatment would adversely affect the mechanical stability of the uranium bar under actual working conditions.

Author's Reply : I have not thought of it but your explanation seems to be good and I am willing to agree.

Mr. R. Choubey, (*N.M.L., Jamshedpur*) : I would like to ask a few questions to Mr. Wyatt. Firstly, as it has been mentioned that fine grain size is preferred for uranium to be used in Atomic reactors, I would like to know why it is so? Whether it is anyway related to the dissimilar nature of the grain boundary and inside of the grains.

Secondly, what is the actual state of stress and temperature to which uranium or other metallic materials are subjected in an atomic reactor and how far creep affects their behaviour.

Lastly, what is the cause of retention of pure sort of preferred orientation in mechanically worked uranium even after recrystallization whereas it is not the case with most other metals and alloys like steels.

Author's Reply : (1) Fuel elements of coarse grained uranium exhibit surface wrinkling when irradiated at temperatures between 0-400°C because of the distortion of the grains. With fine grained uranium this wrinkling is so reduced in scale as to have no harmful effect on the can.

(2) Temperature depends on reactor design. In the Calder Hall type of reactor the operating temperature ranges lies between 180-600°C.

Stress may be due to (1) irradiation growth (2) fission product gases (3) the weight of the fuel element (4) the weight of the fuel elements which it supports and (5) the pressure of the coolant.

Creep has little effect on (1), is probably important in case (2) although correlation is difficult, and should be overcome by engineering design in (3), (4) and (5).

(3) Preferred orientation is retained after the recrystallisation in all metals unless a phase change takes place. Its effects are not apparent in steels because of the symmetrical character of the crystal structure of iron which is cubic, and has three identical axes, whereas those of uranium differ widely.

EXTRUSION OF URANIUM, ZIRCONIUM AND CO-EXTRUSION OF U-Zr BY THE SEJOURNET METHOD

*By Jacques A. Stohr,**

Uranium

The study of the deformability of uranium[1] shows that this metal can be extruded in the upper range of α-phase and in γ-phase.

The extrusion in γ-phase has been carried out by various techniques which differ only in the nature of lubrication and protection for the uranium billet.

The extrusion in α-phase has been carried out by Sejournet method[2] using molten glass as lubricant.

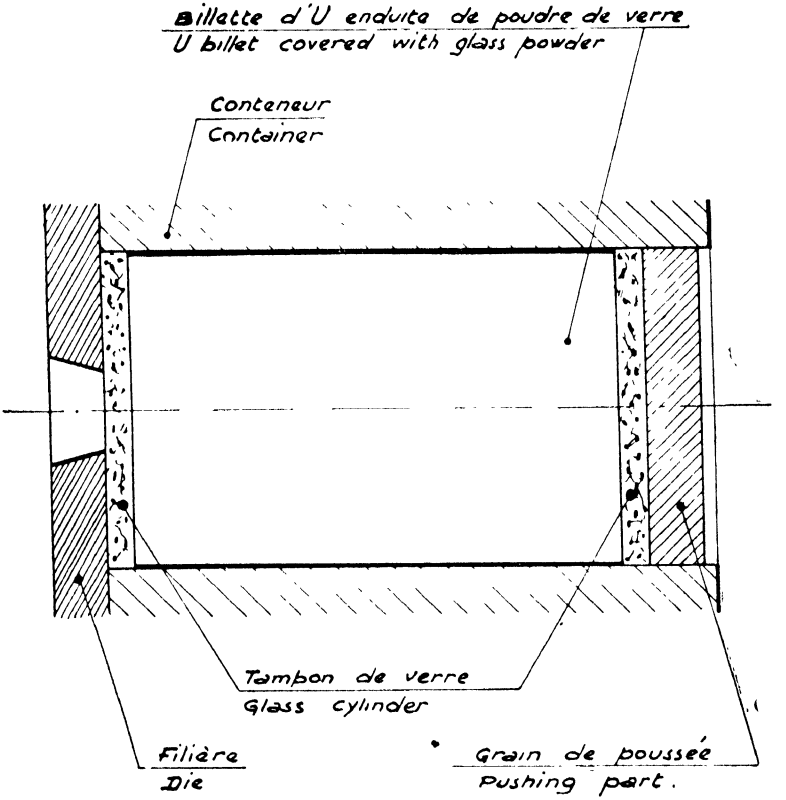


Figure 1

* Commissariat a l'Energie Atomique, Saclay, France.

The billet, heated in a salt bath (barium chloride-sodium chloride) to a temperature of 550° to 600°C is held in the container of the press, after it has been coated with glass powder. A flat cylinder of compressed glass having the same diameter as the billet is interposed between the die and the front surface of the billet; an identical cylinder is interposed between the rear face of the billet and the pushing part (fig. 1).

The nature of glass is so chosen that it would fuse at the temperature of extrusion.

The billets used had a diameter of $\psi_B = 140$ mm, which yielded uranium bars of diameter $\psi_r = 32$ mm and length $l_r = 2.5$ to 3 m. The duration of extrusion varied from 1.5 to 2.5 seconds.

The surface of the bars thus extruded in air was considerably oxidised, which was avoided by receiving the extruded bar in an argon filled receptacle, indentical to that used for the extrusion in γ-phase[1].

The microstructure of the metal thus obtained is considerably different from that of the metal extruded in γ-phase. The ∝ -grains are of very large dimensions, but are polyhedral instead of being shredded as in the case of the metal extruded in γ-phase. The metal is almost free of orientation. The deformation suffered on thermal cyling does not present any difference from that of uranium extruded in γ-phase.

Zirconium

The method has been used for the extrusion of zirconium.

The billet ($\psi = 120$ mm; $l = 120$ mm) prior to extrusion is heated to a temperature of the order of 815°C in a salt bath (barium-and sodium-chlorides) which had been previously deoxidised by heating for 48 hours in presence of zirconium shavings. The extrusion is done in the same manner as that of uranium billet. The nature of glass is, however, different on account of different temperature used in this case.

The metal obtained presents a homogeneous structure. The zirconium undergoes recrystallisation to yield fine polyhedral grains of 10 to 15 μ. Some of the grains are slightly elongated in the direction of extrusion. If zirconium contains carbides, these will be aligned in the direction of extrusion (fig. 2).

It has been possible to obtain by this method discs and tubes in varying ranges of diameter and thickness.

U-Zr Co-Extrusion

The co-extrusion of uranium and zirconium permits the realisation of a bond between uranium used as fuel and zirconium used for sheathing. The conditions of extrusion determine the degree of uranium-zirconium bonding. The billet to be extruded is, in this case, protected by a copper jacket.

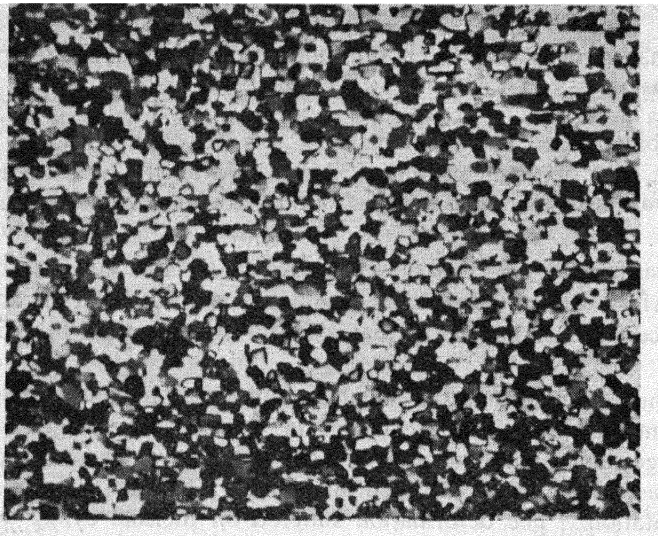


Figure 2. Specimen 1. Extrusion of Zr tube M 919 (6854) x 150

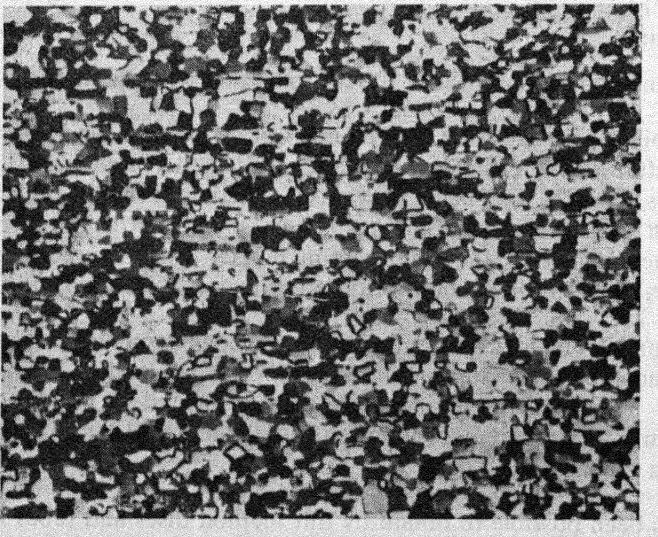


Figure 2. Specimen 3. Extrusion (6855) x 150

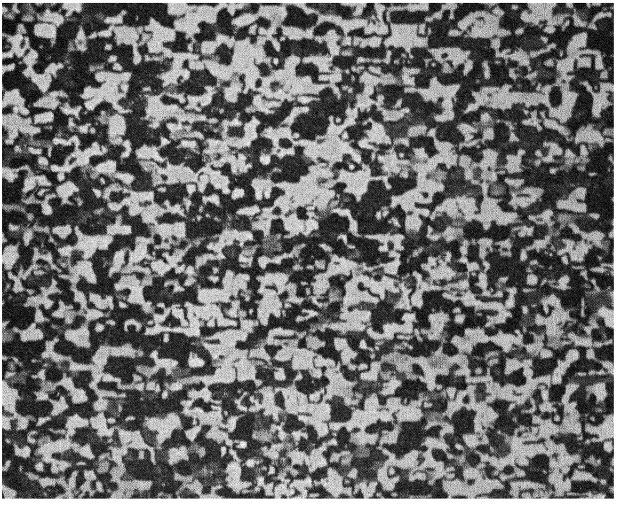


Figure 2. Specimen M 1. Extrusion (6856) x 150

The preparation of this billet consists of :
formation of zirconium can
machining of zirconium can
chemical and thermal treatment (under vacuum) of zirconium can
obtaining uranium billet or uranium alloy by fusion under vacuum[3]
assembly of the billet in the zirconium can
sealing by welding
copper casing

The billet thus prepared (fig. 3) is heated in a salt bath (barium and sodium-chloride) at 600°C and extruded under the same conditions as uranium. Glass is used again as lubricant.

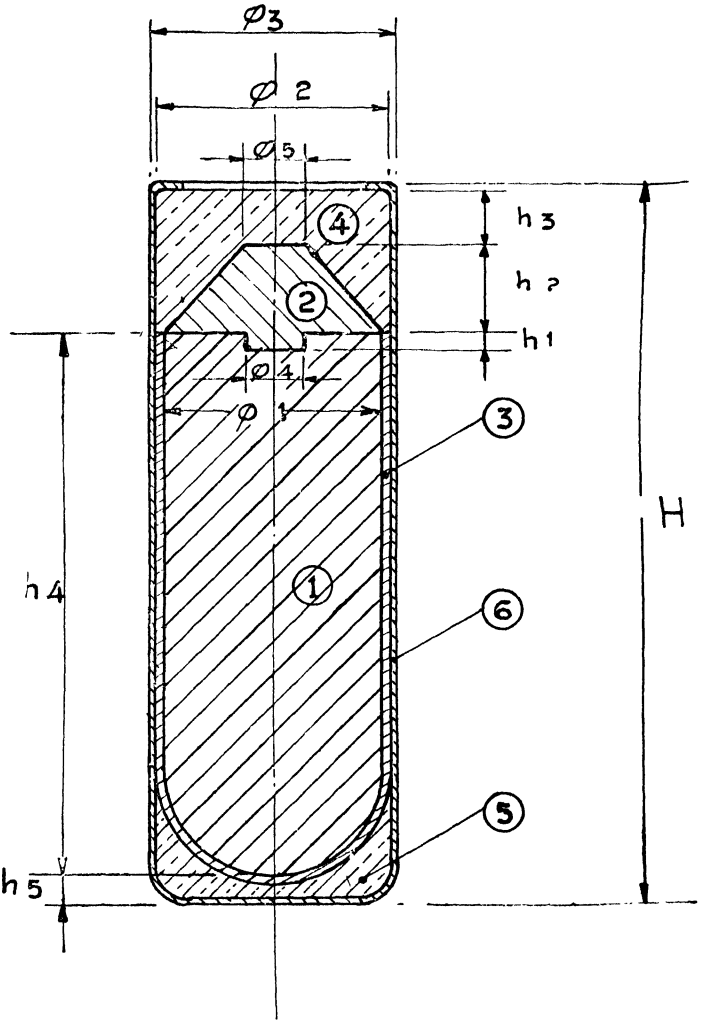
Figure 4 shows the microstructure of a uranium bar sheathed in zirconium, at U-Zr interface. The thickness of the bond is very small. The mechanical resistance of this bond is very high: rupture tests show that the failure may result any where and not preferentially in the bond.

Figure 5 shows the electron micrograph of the same zone.

It is possible to increase the thickness of this zone by carrying the entire assembly to a temperature of the order of 750°C (fig. 6).

The elements of circular or rectangular section have been obtained directly by extrusion in this way.

COMPOSITE U-Zr FUEL ELEMENT BEFORE EXTRUSION



Legend :—

(1) Uranium Billet, (2) Uranium Inset (3) Zirconium, (4) Machined Bronze, (5) Machined Red Copper, (6) Copper Casting.

ϕ_1 .83 Approx.

$\frac{\phi_2 \phi_1}{2} = 4.25$

$\frac{\phi_3 \phi_2}{2} = 1$

$h = 10$, $h_2 = 30$, $\phi_5 = 20$, $h_3 = 10$

h_4 Varies from 221-317, According to the casing, $h_5 = 3$, H Varies from 270-370

Figure 3.

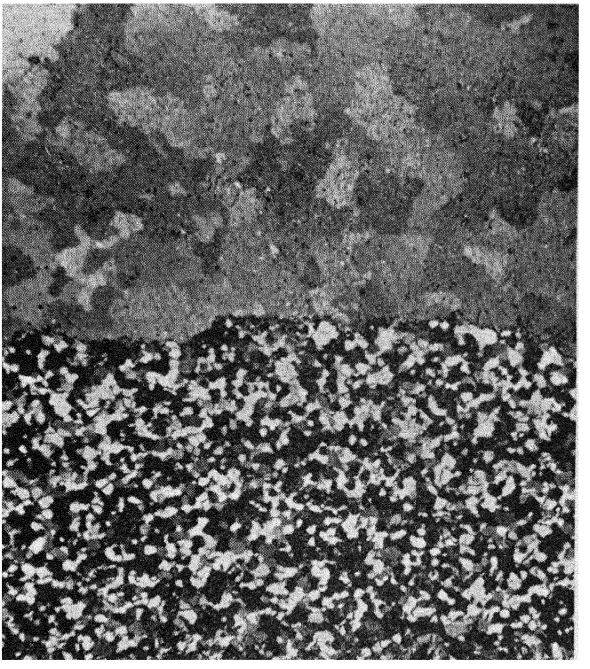


Figure 4.

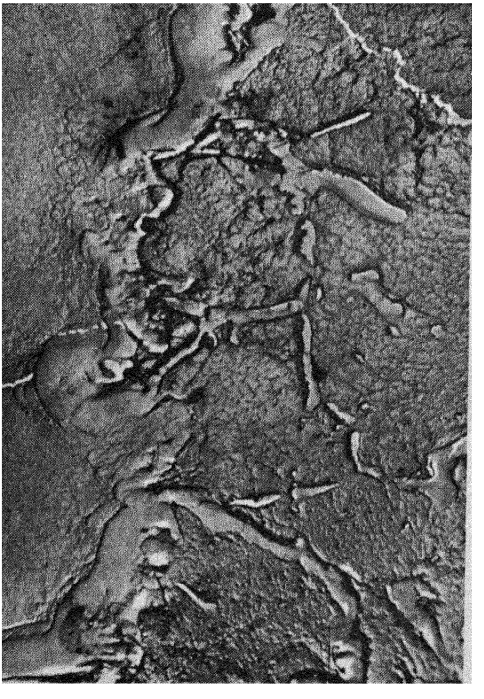


Figure 5

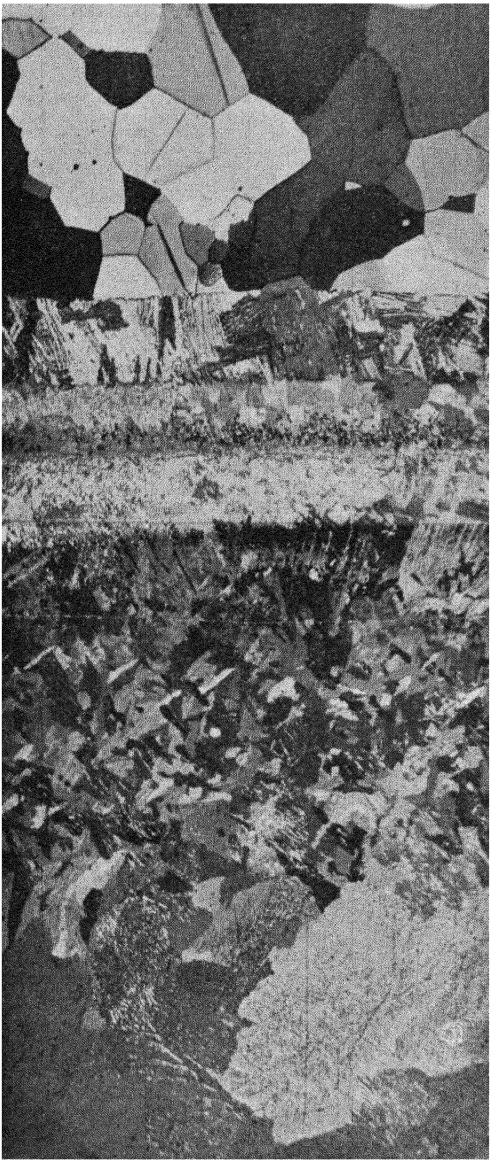


Figure 6

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1. CEA report No. 443 : J. A. Stohr and R. Chevigny. Communication at the Geneva conference 1955, 9|P|351.
   Lloyd : "The extrusion of uranium rod and tube direct from powder." (AERE M|R 1048).
2. J. Sejournet. "The extrusion of steel with glass lubricant." (Society of Civil Engineers of France, 19, rue Blanche, Paris; 22nd June, 1956; F. 12, Page 323).
   J. Delcroix. "Use of glass lubricant for the extrusion of steel. (Centre de Perfectionnement Technique. 28 rue St. Dominique, Paris; F. 3181 of 1.3.1954).
3. Note CAE No. 212: J. A. Stohr "Vacuum melting of uranium."

Discussions

Mr. L. M. Wyatt, (*U. K.*) : Would Dr. Caillat like to comment on the difference between French practice as described by Dr. Stohr and American practice described in "Bomb Reduction, Forging and Extrusion of uranium and uranium alloys". J. A. Fellows, Mallinkrodt, 25-10-57.

The French extrude in the γ-phase without glass lubricant, and with glass lubricant in the α-phase. Mallinkrodt extrude in the α-phase without glass and with glass in the γ-phase. The explanation may be that the Americans use a lead cone of steel in the α-and a steel die in the γ-, which could alloy with uranium, whereas the French use a hard metal die.

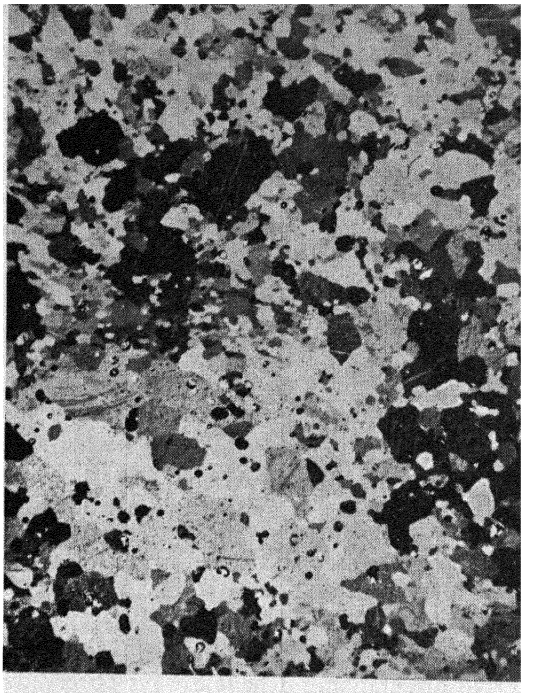
I do not understand how it is possible to extrude in the α-phase without getting preferred orientation. I have always observed fine grained oriented structures after extrusion and this is confirmed by Mallinkrodt. Can it be that the uranium is in the β-phase at the moment of passing through the die?

Dr. R. Caillat, (*France*) : We can equally well use glass in the extrusion in γ-phase. I am also of the opinion that glass can then protect uranium, to a certain extent, either from the contamination through steel dies or from the oxidation by air. At the extrusion temperatures in γ-phase, a protection is particularly necessary.

Concerning the orientation of uranium crystals in the bar extruded in α-phase, a preferential direction is not distinctly evident. But I will not go to such an extent of saying that these orientations are perfectly distributed in all directions, the less so, when the bars are made up of big grains.

Finally, to answer your last question, the deformations undergone by uranium in the course of extrusion in α-phase can in fact involve an elevation of temperature and the passage from α-β transformation point.

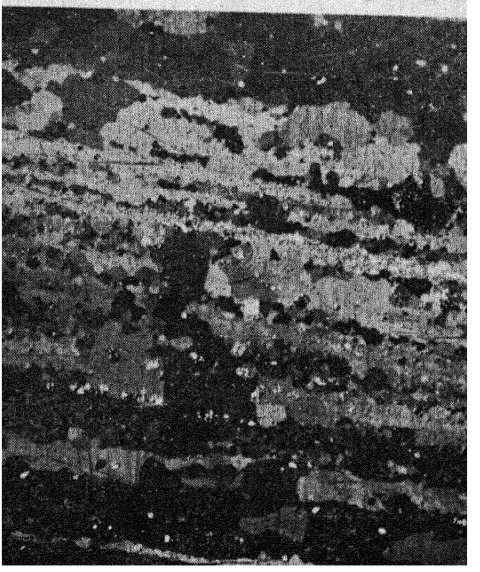
The operation is then affected : the β-phase is brittle. The conditions of extrusion should be foreseen to avoid that. The lubrication by glass forms part of these conditions.



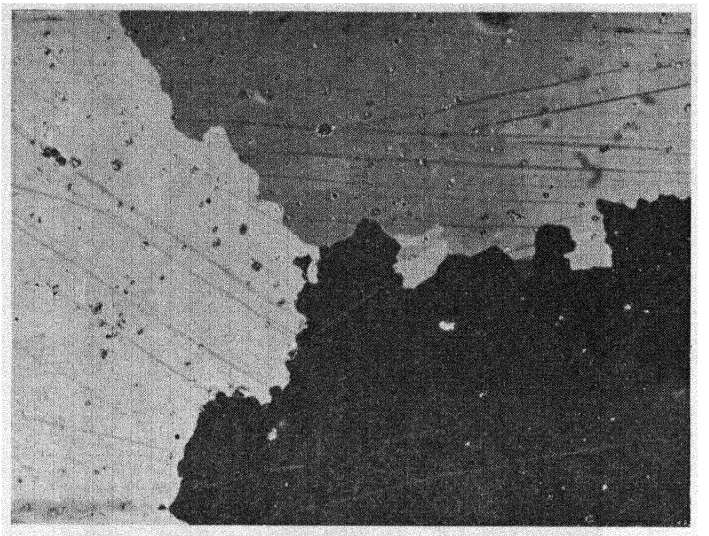
8143

8148

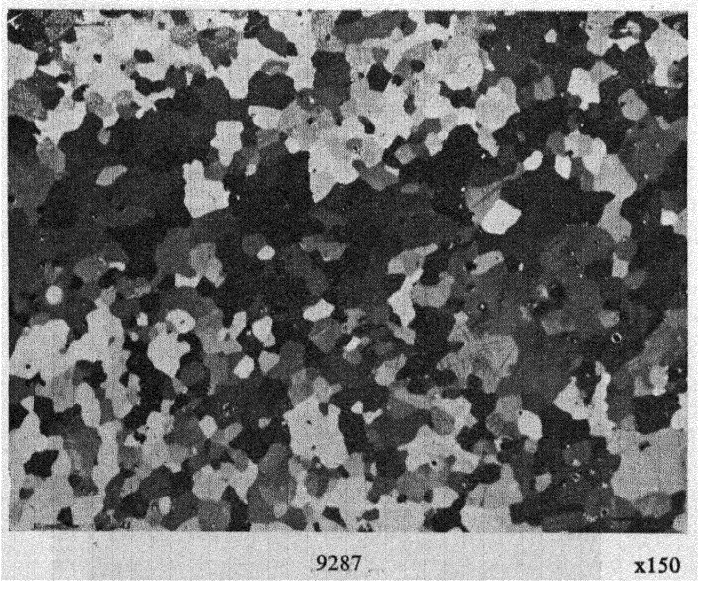
8149



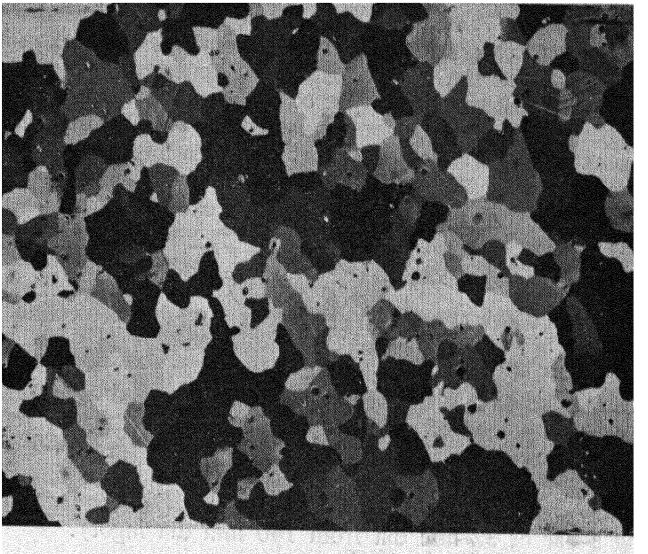
8150



9284 x150

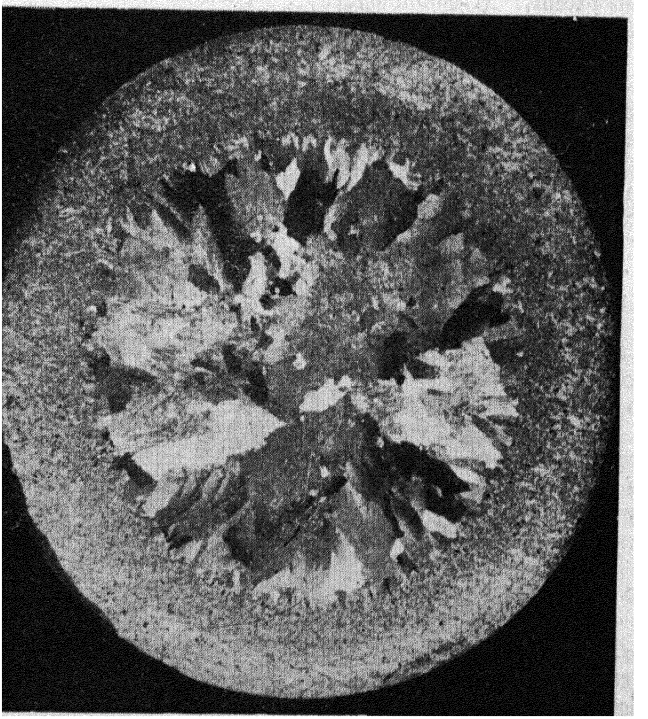


9287 x150



x150

9286



x4

Mr. R. Choubey, A question had previously been raised by Mr. Wyatt about the use of glass as lubricant in the α-stage extrusion of uranium, as given in Dr. Stohr's paper. It appeared to him as quite different from the American practice of using glass in the γ-stage. Now I would like to enquire whether the American practice of using glass in γ-stage extrusion is aimed at protecting the die materials from being affected with the extruded metal at higher temperature rather than for lubricating purposes, which is so, in α-range extrusion of uranium.

Dr. R. Caillat, (*France*) : Yes. I think it is to stop oxidation.

Mr. L. M. Wyatt, (U.K.) : Yes. It is for the protection of die material.

Mr. H. C. Katiyar, What will be the effect of speed of extrusion on the physical properties of extruded uranium with particular reference to grain size orientation and hardness ?

What was the capacity of the extrusion press (i.e. tonnage used for extruding a bar of 32 mm dia from 140 mm dia ingot)?

Author's Reply, (*Communicated*) : There is no effect of extrusion speed on the physical and mechanical properties of uranium, in case of γ-extruded uranium (950°C).

In case of α-extrusion in the range of 550-600°C, the extrusion speed acts on the grain size. It may be possible to obtain fine grain size, especially in the external zone. In that case unfortunately the metal has a great preferred orientation. So a β-treatment is necessary after extrusion.

For γ-extrusion (950°C), the press capacity was 80 tons, for extruding a rod of 32 mm dia. from an ingot of 140 mm dia.

For the same size of rod and ingot, the press capacity increases at a value of 1000 to 1500 tons, in the case of α-range (550-600°C) extrusion with glass as lubricant, and a ram speed of about 10 meters/min.

Since my report of October, 1957, we tried successfully the α-extrusion of uranium with a mixture of graphite and resin as lubricant. The ram speed was considerably lower than in our first experiment, about 240 mm/min. The ingot was heated before extrusion in an argon furnace. In that case, we observed a significant action on the grain size, due to the reduction rate.

The micrographs (8143, 8148, 8149, 8150) were obtained on a rod extruded in the α-phase with a reduction rate of 25/90, and the micrographs (9284, 9286, 9287) alongwith a macrograph, with a reduction rate of 28/90.

RECENT DEVELOPMENTS IN THE PHYSICAL METALLURGY OF PLUTONIUM

By D. M. Poole & M. B. Waldron *

This paper presents recent developments in the metallurgy of plutonium and its alloys and deals mainly with work carried out at the Atomic Energy Research Establishment, Harwell. Where information was obtained elsewhere this fact is noted in the text. Sections 2 and 3 briefly review health hazards and information available up to 1956; these aspects have been fully covered by Coffinberry and Waldron's article "The Physical Metallurgy of Plutonium"[1] to which reference should be made for further details. Information obtained since 1956 is presented in section 4 and briefly discussed in section 5.

Health Hazards

Plutonium poses a number of problems to those who work with it and these are considered below.

(a) It is fissile and precautions must be taken to ensure that a critical mass is not accidentally assembled. This is a question of careful design of apparatus and control of potentially dangerous quantities of material.

(b) Certain isotopes of plutonium and some impurities present in the massive metal emit sufficient γ-radiation to cause a hazard; normally this can readily be overcome by limiting the time for which the metal is handled by a given worker or by ensuring that close contact is avoided. If plutonium is alloyed with a light element, such as beryllium, (α, n) reactions may result in sufficient neutron emission to necessitate shielding and remote handling techniques.

(c) Plutonium is pyrophoric when finely divided or when alloyed with certain other elements; this means that inert atmospheres must often be employed and great care taken to avoid the initiation of fires.

(d) The α-activity of plutonium-239 (the isotope normally predominant) does not result in a significant external radiation hazard from the massive metal since the range of the α-particles is small and they are stopped by the thickness of a rubber glove or as little as 45 microns of body tissue. However, if plutonium is absorbed into the body a large proportion of it remains in the bones for a lifetime and then the α-particles cause grave damage resulting in leucaemia and cancer; the toxicity of plutonium is extremely high and the maximum amount which can be allowed to accumulate in the body is set at 0.6 micrograms—a single small dust particle. Almost all the plutonium entering the blood stream is retained in the body so that cuts from the metal or from contaminated articles must be avoided at all costs. About

* Atomic Energy Establishment, Harwell, U.K.

20% of inhaled plutonium is retained in the body and this cumulative effect means that only extremely low levels of airborne contamination can be tolerated in the laboratory atmosphere—in fact the maximum permissible level for plutonium is 350 million times less than that for hydrogen cyanide gas. The situation is aggravated by the speed at which plutonium oxidises under normal conditions to produce very finely divided powder which rapidly becomes airborne.

The way in which this problem of airborne hazard is tackled varies from country to country and also from establishment to establishment. For example, the approach adopted in Britain keeps all plutonium alloys inside air-tight glove-boxes which contain all the necessary equipment for research; these boxes are usually constructed of steel and perspex, have long rubber or neoprene gloves sealed onto one or more faces, are maintained at a pressure slightly below that of the laboratory and are often filled with argon to prevent oxidation of the plutonium. (Fig. 1.) Passage of articles into or out of the boxes is carried out by a plastic bag technique which maintains complete isolation of the box atmosphere the whole time. Normally all operations are carried out by manipulation through the long rubber gauntlets but occasionally the services of "frog-men" are required. These are men in pressurised suits who operate in a highly active work-shop into which the boxes can be taken and dismantled for servicing; alternatively the box can be sealed to the wall of the active workshop and a panel then removed so that the interior can be reached by the pressurised suit operatives. (Fig. 2).

American practice at the Los Alamos laboratories, on the other hand, involves occasional exposure of alloys and contaminated equipment to the laboratory atmosphere. The system requires scrupulous cleanliness in working enclosures which are opened for access; care must be taken in selecting the surface condition or the type of alloy which is to be removed to the open laboratory for micro-examination or other non-destructive testing.

Despite these difficulties a considerable volume of data on plutonium and its alloys is now available in the declassified literature and is reviewed in the next two sections.

Work Published up to 1956

Plutonium is virtually non-existent in nature and not until 1943 did the first significant quantities become available from the neutron irradiation of uranium. The first minute beads of metal were produced at the University of Chicago and gave indications of the strange properties of plutonium—some had a density close to 19 g./c.c. and were brittle, whereas others were ductile and had a density of about 16. Larger amounts were available by 1944 when thermal analysis work at Los Alamos indicated that five different modifications (designated α, β, γ, δ and ϵ) occurred in the solid state! This conclusion was supported by dilatometer work in the United States and also in Great

Britain. The British dilatometer and thermal analysis curves showed traces of yet another phase, but this evidence could not be substantiated by high temperature X-ray work. However, X-ray investigations on both sides of the Atlantic confirmed the existence of five phases and showed that the α, β and γ phases have complex structures and the δ and ϵ phases are face-centred cubic and body-centred cubic respectively.

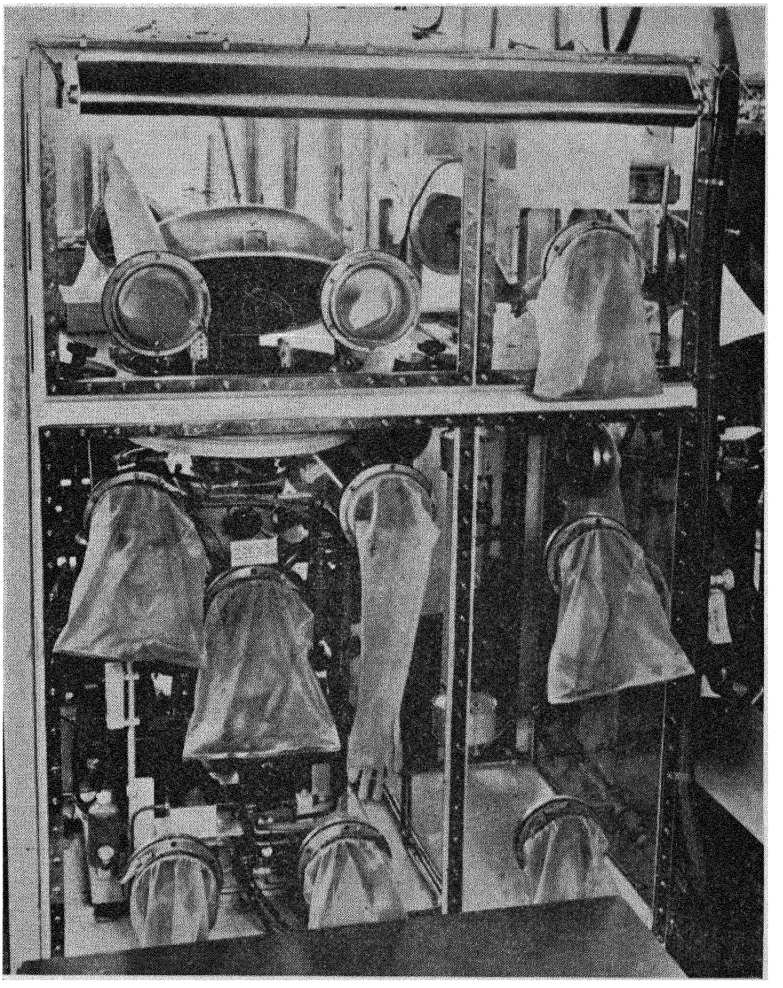


Fig. 1.—Typical glove box at Harwell; note upper working space and lower compartment for pumping equipment

The availability of material of higher purity in America and a refinement of their dilatometer technique revealed in 1953 a sixth phase

which was designated δ′ ; the existence of this phase was confirmed by the appearance in the very pure metal of a tetragonal structure which is a slightly distorted form of the face-centred cubic δ structure; however it is crystallographically more correct to describe the structure in terms of a body-centred tetragonal cell.

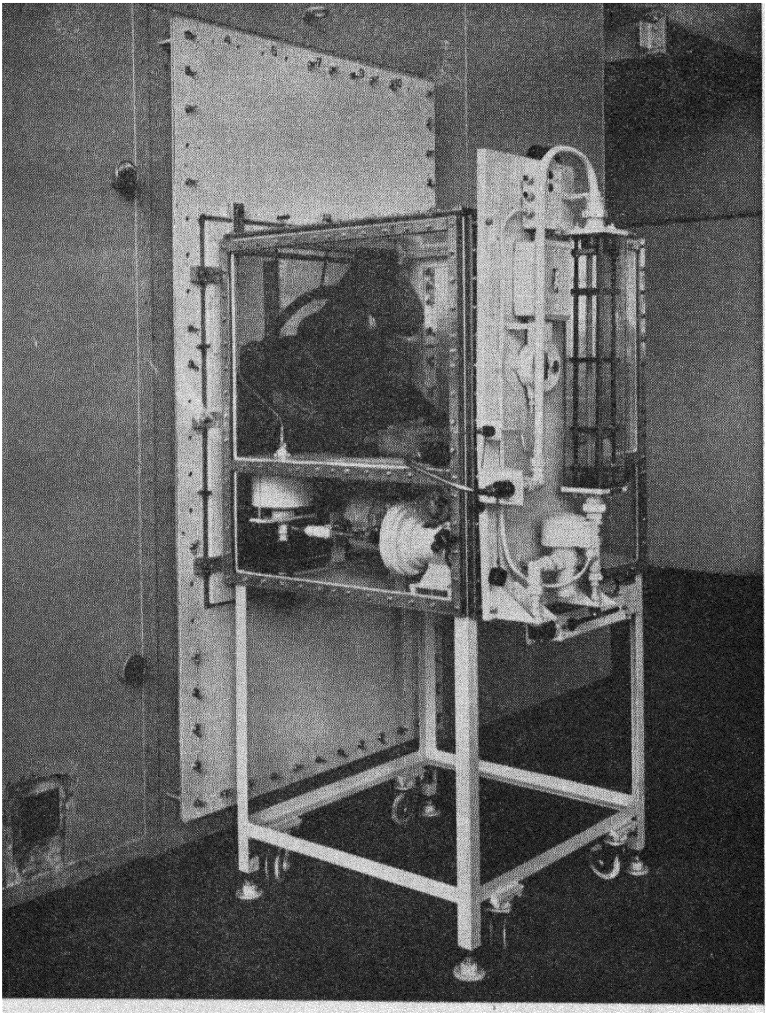


Fig. 2.—Glove box sealed to wall of active workshop and being serviced by pressurized suit operative

Further confirmation of the existence of 6 phases came in the Russian paper[2] published in 1955; which included thermal analysis and

magnetic susceptibility traces which clearly showed five solid state phase changes.

The temperature ranges of stability, the crystal structures and the densities of the six plutonium phases are presented in Table I. The figures taken are from American thermal analysis and X-ray work.

Table I—Transformation Temperatures, Crystal Structures and Densities of Plutonium Phases

Phase	Stability Range °C	Crystal Lattice	Cell Dimensions A	Calc. Density g/c.c.
α	? to 122	Monoclinic 16 atoms/cell	a = 6.1835 ± 0.0005 b = 4.8244 ± 0.0005 c = 10.973 ± 0.001 β = 101.81° ± 0.02° at 21°C	19.816
β	122 to 203	Unsolved pattern		
γ	203 to 317	Face centred orthorhombic 8 atoms/cell	a = 3.1587 ± 0.0004 b = 5.7682 ± 0.0004 c = 10.162 ± 0.002 235°C	17.14
δ	317 to 453	Face centred cubic 4 atoms/cell	a = 4.6371 ± 0.0004 at 320°C	15.92
δ'	453 to 478	Body centred tetragonal 2 atoms/cell	a = 3.327 ± 0.003 c = 4.482 ± 0.007 at 465°C	16.00
ε	478 to 639.5 ± 2	Body centred cubic 2 atoms/cell	a = 3.6361 ± 0.0004 at 490°C	16.51

Many other physical properties of the plutonium phases are reviewed in Coffinberry and Waldron including expansion coefficients, resistivity data, elastic properties of α-plutonium, and compressibility, thermodynamic and magnetic data. Of particular interest are the negative coefficients of thermal expansion of δ and δ' which are accompanied by positive electrical resistivity coefficients, whereas the other phases have positive expansion and negative resistivity coefficients. The occurrence of a negative coefficient of thermal expansion in an isotropic material is unique and has been the subject of theoretical discussions by Lee and Mardon[3] and by Varley[4].

One feature which complicates the physical properties of plutonium is the sluggishness or absence of some of the transformations on cooling and certain anomalous features of the $\gamma \rightarrow \beta$ phase change. These

result in variable properties which depend on the thermal history of the specimen and which for example can lead to widely varying room temperature densities for massive plutonium.

The first indications of the alloying behaviour of plutonium came from the frequency with which the δ-phase was stabilised by the presence of impurities resulting in the ductility and low density of the early samples of metal.

The only phase diagram data which was declassified in 1956 was that obtained by Russian workers and published by Konobeevsky[2]. The diagrams concerned are those of plutonium with beryllium, lead, vanadium, iron, manganese, nickel and osmium. All but the osmium and iron diagrams show no solid solubility at either end of the diagram; some solubility of iron in δ and ε plutonium and of osmium in ε plutonium are indicated.

Russian, Canadian, British and American data on the crystal structures of 62 plutonium binary compounds have been collated by Coffinberry and Waldron. A number of these compounds are of well known structure types, e.g., Laves phases or are isostructural with the corresponding uranium or thorium compounds.

Recent Developments

(a) *Physical Properties of Plutonium* (*i*) *Phase changes and Dilatometric Behaviour*[5]: In recent months samples of plutonium purified by zone melting[6] have become available and have been subjected to thermal analysis and dilatometry. This metal is of comparable purity to the American high purity material and clearly shows the presence of the six phases. The dilatometer curve on heating is shown in Fig. 3 and the results of both experiments, which were run at ~1°C/minute heating rate, are presented in Table II.

Table II—Transformation Temperatures and Expansion Coefficients of High Purity Plutonium

Phase	Transformation Temperature on heating °C		Linear Coefficient of Thermal Expansion	
	Thermal Analysis	Dilatometry	$\times 10^6$/°C	
α	126±2	133	+67	(80—120°C)
β	209±3	208	+41	(160—200°C)
γ	316±2	306	+35	(220—280°C)
δ	456±5	460	— 8.6	(340—440°C)
δ′	484±2	476	—596*	(470°C)
ε	641±2	634	+15	(490—550°C)

* Value probably high due to continuing transformation.

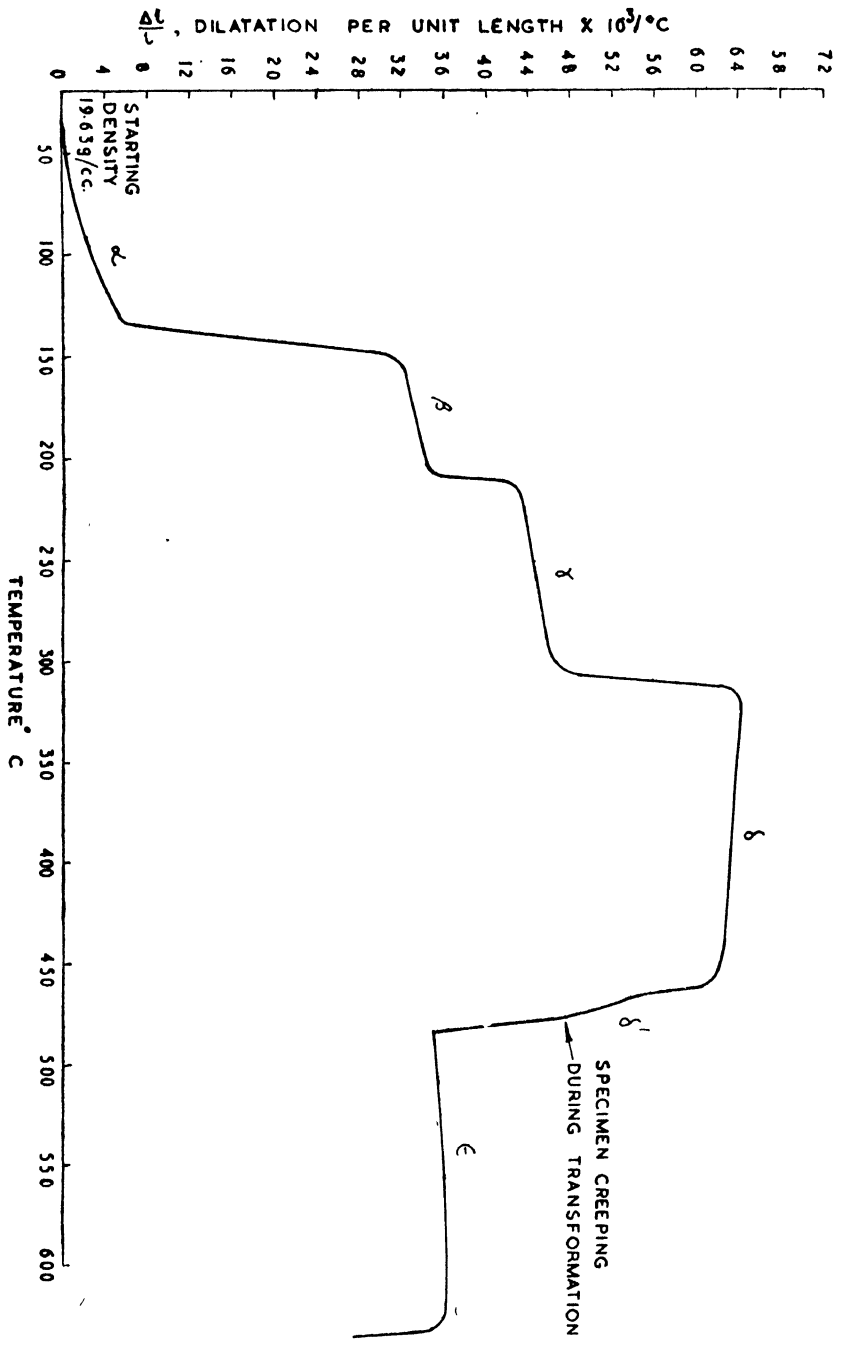

Δl/l, DILATATION PER UNIT LENGTH X 10³/°C
0 4 8 12 16 20 24 28 32 36 40 44 48 52 56 60 64 72
STARTING DENSITY 19.63 g/cc.
α
β
γ
δ
δ'
ε
SPECIMEN CREEPING DURING TRANSFORMATION
50 100 150 200 250 300 350 400 450 500 550 600
TEMPERATURE° C

Fig. 3.—Dilatition curve of high purity plutonium

The hysteresis effects associated with the phase changes are illustrated by the values of the transformation temperatures obtained on thermal analysis with a heating rate of 4°C|min and a cooling rate of 1°C|min. as shown in Table III.

Table III—Hysteresis of Phase Changes in High Purity Plutonium

Transformation	Transformation Temperature°C	
	Heating 4°C|min.	Cooling 1°C|min.
$\alpha \leftrightharpoons \beta$	142±5	Not determined
$\beta \leftrightharpoons \gamma$	238±5	150
$\gamma \leftrightharpoons \delta$	325±5	230
$\delta \leftrightharpoons \delta'$	451±5	Uncertain
$\delta' \leftrightharpoons \epsilon$	481±3	487±2

(ii) *The* $\alpha \leftrightharpoons \beta$ *transformation*[7] : Dilatometric studies have been made of the isothermal $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations and the results are shown in Fig. 4. These indicate that the true transformation temperature is 117±2°C at which temperature the incubation period is of the order of 10 years.

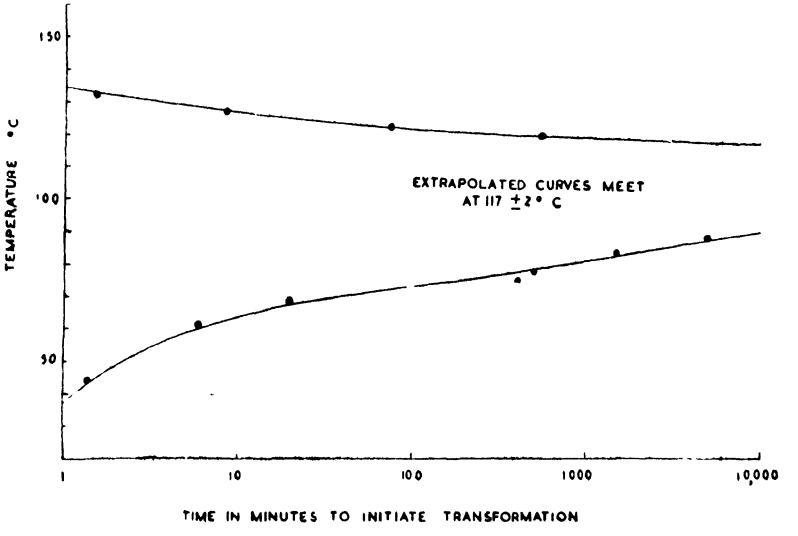


Fig. 4.—Kinetics of $\alpha \leftrightharpoons \beta$ transformation

(iii) *Thermal Conductivity of* α *-Plutonium*[8] : This property is currently being measured on a bar of plutonium 5″ long x1″ in diameter with one end projecting into a recirculating coolant heat sink. The self-heating effect establishes a temperature gradient down the specimen which is measured by attached thermocouples and enables the

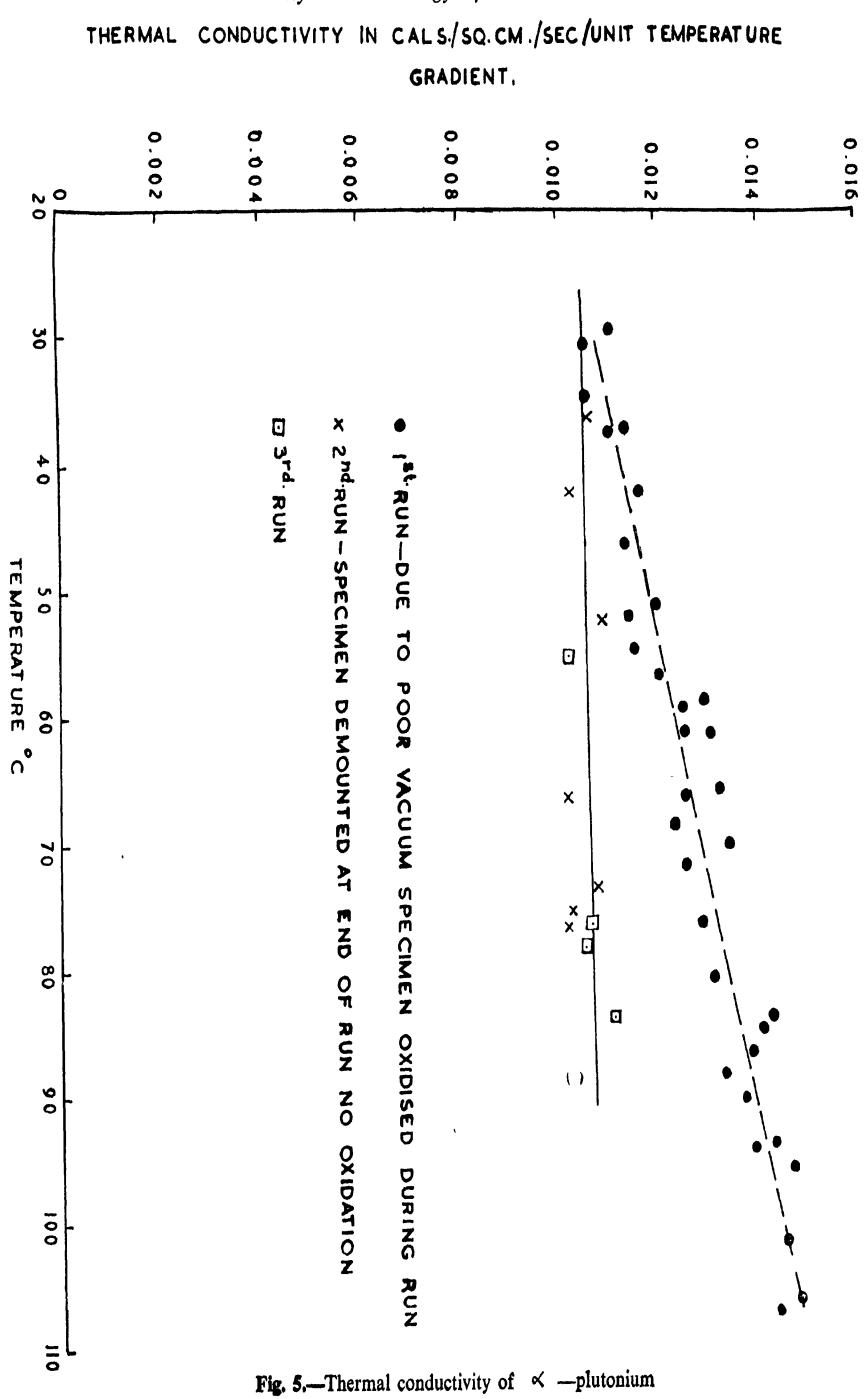


Fig. 5.—Thermal conductivity of ∝ —plutonium

conductivity to be calculated. The results of three runs determining the value at various temperatures are shown in Fig. 5. The first run is believed to have yielded erroneous results due to oxidation and consequent faulty temperature measurements; the second and third runs indicate a value of 0.010_5 cals|sq. cm|per sec|°C at 40°C with almost no temperature dependence.

(iv) *Specific Heat of* α *-Plutonium* : Using an adiabatic self-heating method workers at Aldermaston[9] have established a value for the specific heat at constant pressure of 0.032 cal|gm|°C.

An approximate determination has been made at Harwell[10] by quencing a small cylinder of plutonium from 80°C into an oil bath at room temperature and following the temperature rise of the bath : the value of Cp so obtained was 0.036 ± 0.0015 cals|gm|°C.

(v) *Magnetic Moment of* Pu^{239}[11]: Electronic paramagnetic resonance studies have shown that the nucleus of Pu^{239} has spin $\frac{1}{2}$ and a nuclear magnetic moment of 0.2-0.6 nuclear magnetons. No resonance has been detected in the range 0.27-0.58 nuclear magnetons.

(vi) *Young's Modulus of* α *-Plutonium*[12] : The adiabatic value of Young's modulus for pure plutonium at room temperature has been obtained by determining the resonant frequency of a bar in transverse oscillation. The value obtained was $8.60 \times 10''$ dynes|cm^2 or 12.5×10^6 lbs.|in^2.

Tensile stress|strain curves at room temperature obtained at Aldermaston[9] give a value of $8.2 \times 10''$ dynes|cm^2 ; in compression the value of the modulus obtained was $9.9 \times 10''$ dynes|cm^2 with Poisson's ratio equal to 0.4.

(b) *Alloying Behavior* : A number of constitutional studies of plutonium based systems have been made over the last two years. These include :—

(i) *The Plutonium-Uranium System*[13] : This system is currently being studied and a provisional diagram is shown in Fig. 6. The diagram is based largely on thermal analysis data accumulated with the aid of automatic differential thermal analysis equipment operating on previously arc-melted alloys. The system shows continuous solubility of ϵ -plutonium and γ -uranium into which the η -phase intrudes almost up to the solidus in the middle of its stability range. The η-phase has a wide stability range and a complicated structure containing 52 atoms in the unit cell; on cooling η transform to another phase ζ -which also has a wide stability range and complicated structure. The solubilities of plutonium in α and β-uranium (maximum 15 and 19 at .% respectively) exceed those of any other known element. The δ'-plutonium phase dissolves about 1% uranium and shows clearly on the diagram which gives further confirmation of the existence of this sixth phase of plutonium.

(ii) *The Plutonium-Thorium System*[15] : X-ray, metallographic, and combined dilatometry and thermal analysis studies have been used to

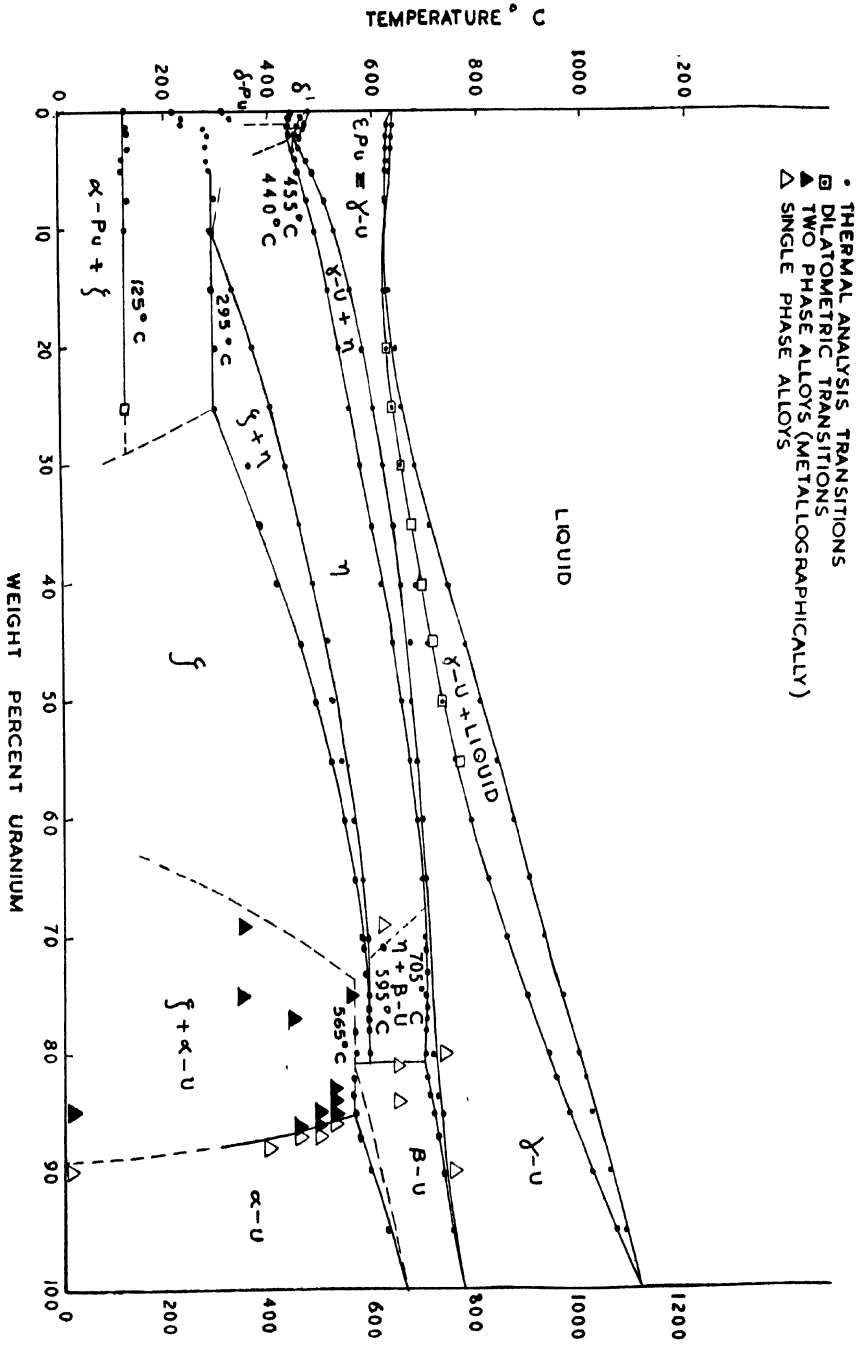


Fig. 6—The plutonium—uranium equilibrium diagram.

establish the principal features of this system (Fig. 7). The solubility of plutonium in thorium is almost 50 at.% at its maximum; lattice parameter and density curves indicate an apparent atomic radius of 1.697 Å for plutonium in solution in α-thorium. The compound close to the composition Pu_2Th forms only sluggishly on cooling and this feature complicated the establishment of the form of the diagram; its structure is tentatively identified as orthorhombic with a=9.820, b=8.164 and c=6.681 Å. There is some solubility of thorium in δ—and ε-plutonium.

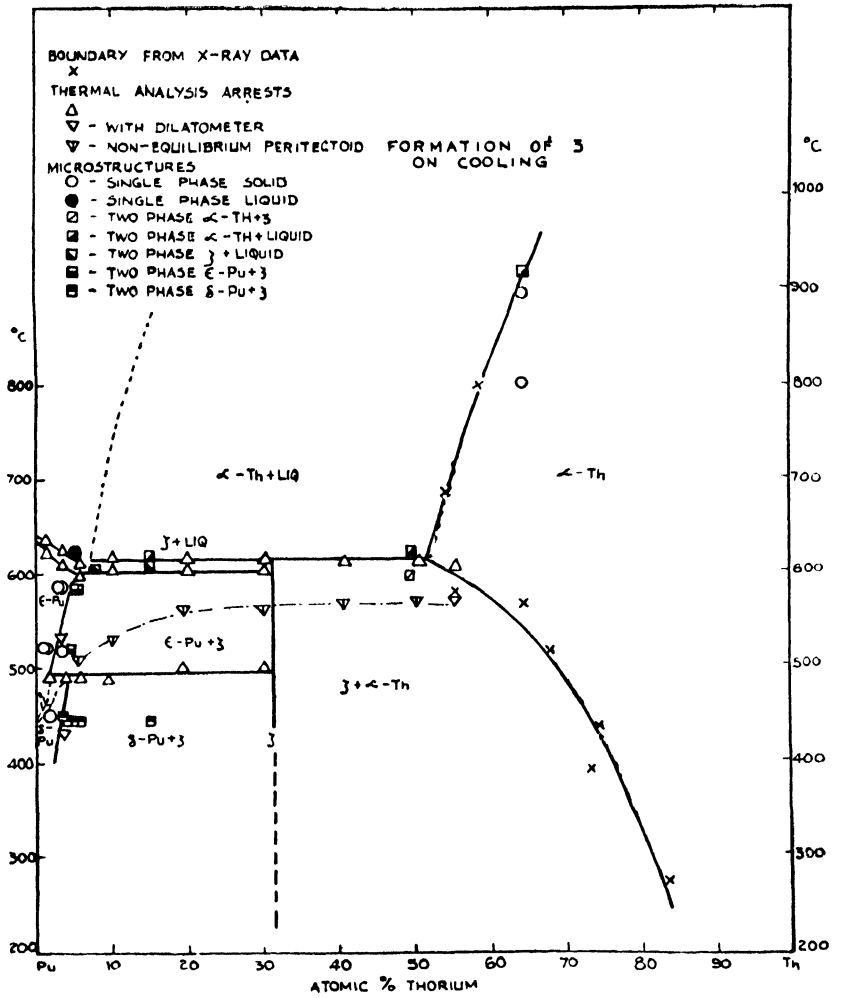


Fig. 7.—The plutonium—thorium equilibrium diagram

(iii) *The Plutonium-Iron System*[16]: The diagram published by Russian workers was based on micro-metallurgical techniques and in

particular lacks detail at the plutonium-rich end; hence the whole system has been re-investigated at Harwell. Using thermal analysis, dilatometry, X-ray and metallographic techniques, the diagram shown in Fig. 8 has been established. The existence of the compounds $PuFe_2$ and Pu_6Fe ($MgCu_2$ type, a=7.189±0.002 A; body centred tetragonal, a=5.349±0.003, c=10.405±0.005 A resp.) is confirmed. The plu-

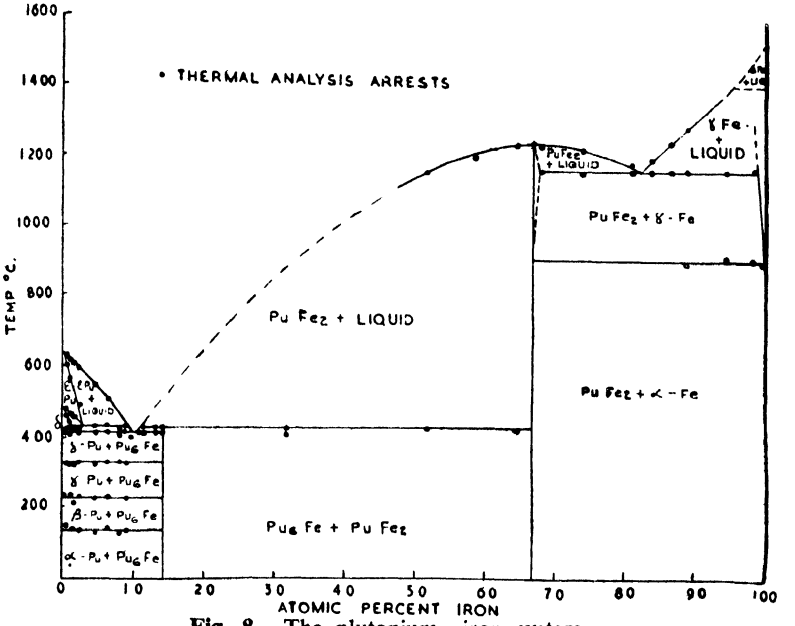

• THERMAL ANALYSIS ARRESTS
TEMP °C.
ATOMIC PERCENT IRON
Pu Fe₂ + LIQUID
Pu Fe₂ + γ - Fe
Pu Fe₂ + α - Fe
Pu₆ Fe + Pu Fe₂
γ Fe + LIQUID
PuFe₂ + LIQUID
δ - Pu + Pu₆ Fe
γ Pu + Pu₆ Fe
β - Pu + Pu₆ Fe
α - Pu + Pu₆ Fe

Fig. 8.—The plutonium—iron system

tonium-rich end has been studied in detail and shows an unusual feature in binary equilibrium diagrams, namely the intrusion of a horizontal liquid and solid field between two solid fields due to the decomposition on cooling of solid ε Pu into δ-Pu and liquid; this means that if an alloy with one or two percent iron is heated it partly melts at 413°C to form δ + liquid and then solidifies again at 430°C to ε + 6 and finally passes through the normal solidus and liquidus lines into the wholly liquid field.

(iv) *The Plutonium-Zirconium System*[17]: Investigation of this system is still in progress but it appears that there is continuous solubility between the two high temperature b.c.c. phases ε-plutonium and β-zirconium. At intermediate temperatures there is an extensive single phase region based on the face centred cubic δ-plutonium phase which extends to 70 at.% at 600°C. At lower temperatures two intermediate phases separate rather sluggishly at compositions close to 20 at.% and 67 at.% zirconium. The structure of the former is not known but is probably complex, while the latter is hexagonal with a structure similar to UZr_2 (space group $P\bar{6}$ m 2; a=5.055 Å, c=3.123 A).

The solubility of plutonium in α-zirconium (max. 13 at.%) exceeds that of any other metal with the exception of titanium and hafnium which show continuous solubility between the hexagonal α-forms.

(v) *Plutonium-Uranium-Molybdenum* : This system is also in the course of investigation at Harwell. One feature which has been established is that extensive additions of plutonium can be made to the γ uranium-molybdenum solid solution without the formation of a second phase.

(c) *Fabrication Techniques* : Plutonium is amenable to all the usual methods of fabrication—argon-arc or resistance melting, casting, machining, extrusion, etc.—provided that great care is taken to prevent oxidation. An excellent example of this proviso is the successful production of clean extrusions of plutonium[19] ; until an argon atmosphere of extreme purity was attained in the extrusion chamber any products were irregular and heavily oxidised. The necessary degree of atmosphere control can, however, be attained for plutonium-rich materials even on a production line such as was necessary for the manufacture of the plutonium charge for the fast reactor Zephyr.

If the plutonium is in the form of a relatively inert compound in an inert matrix, or if the plutonium bearing material can be completely sheathed in an inert material, atmosphere control and health restrictions can be relaxed or dispensed with.

One example of the sheathing technique is the production of plutonium oxide-thorium powder compacts by hydrostatic pressing[20]. The powders were mixed and loaded into a rubber tube under glove-box conditions ; the tube was then sealed in a plastic bag, detached from the box and subjected to hydrostatic pressure under entirely non-active conditions without any spread of activity occurring.

The plutonium-aluminium fuel elements being prepared at the Atomic Weapons Research Establishment, Aldermaston[21] illustrate the relaxation of atmosphere control which is possible when the plutonium is in an inert matrix. The alloy consists of $PuAl_4$ compound particles in a $PuAl_4$|Al eutectic matrix; after melting and casting in a resistance furnace in an argon atmosphere the alloy is hot-rolled in an air-filled box to form plate elements which are later sheathed in aluminium.

(d) *Irradiation Properties*[22] : The irradiation properties of some alloys containing plutonium have been investigated to burn-ups of 0.2-0.8% of all atoms. Irradiation behaviour is currently assessed by a consideration of the R value (% decrease in density|% burn up of all atoms) and some values of this parameter for irradiations at 500°C and 700°C are presented in Table IV.

Table IV—Irradiation Behaviour of Plutonium and Uranium Alloys

	R Value * 500°C	700°C
Unalloyed U	34†	33
U—7½ at .% Pu	17	28
U—10 at .% Pu	53‡	70‡
U—28 at .% Mo	6	4
U—28 Mo-6½ at .% Pu	45‡	12
Th—47 at .% U	13.6	—
Th—15 at .% Pu	22	—
Zr—20 at .% U	8.5	—
Zr—40 at .% Pu	6	—

† Mean of three specimens. ‡ Estimated from dimensional changes.
* R = % decrease in density | % burn up of all atoms.

These results suggest that the addition of modest quantities of plutinium to thorium, uranium or uranium—28 at .% molybdenum may yield a satisfactory alloy. Dilution of plutonium with zirconium results in a particularly satisfactory alloy in view of the low R value obtained and also the low neutron capture cross-section of zirconium.

Discussion

Plutonium is a member of the series of elements in which the 5f electronic shell is being filled whilst the number of electrons in the 6d and 7s shells remains roughly constant. The series of elements is commonly called the 'actinides" which implies a basic valency of 3, just as the lanthanides also have a basic valancy of 3. However the 5f, 6d and 7s levels are so close that electron interchange can easily take place and the elements are charcterised by variable valencies.

The variable valency of these elements is clearly shown by their chemical behaviour and also by the variation in atomic size shown by the pure metals. Zachariasen[23] has collated the available data on the atomic radii of the actinides ; by making the assumption that the valency of thorium is four, he has applied the Pauling formula to relate valency and atomic radius of these elements. If his relations are applied to plutonium the following values appear for the allotropes of the pure metal.

	Radius	Valency
α	1.53 A	5.7
β	1.58	5.1
γ	1.58	5.1
δ	1.65	4.5
ϵ	1.61	4.8

It thus appears that plutonium normally has a greater valency (and hence a smaller radius) than the basic actinide value of 3 ; the body centred cubic forms of neptunium and uranium also appear to have valencies close to six on this scheme. Americium, however, has a large radius corresponding to a valency of 3.1-close to the basic actinide valancy.

Friedel[24] has pointed out that the behaviour of the elements francium, radium, actinium and thorium is typical of a transition series with s, d hybrid bonds whereas the double hexagonal cell of americium is characteristic of rare earth metals with a stable f shell. The properties of the intermediate elements uranium, neptunium and plutonium do not suggest either transitional or rare earth behaviour and Friedel proposes that these properties are connected with hybridisation of the 5f-orbitals, which are just beginning to fill up, with the 6d and 7s ; he further explains some of the directional nature of bonding in these elements, e.g. α -uranium, in terms of the hybridisation of symmetrical d and unsymmetrical f orbitals. Friedel is thus suggesting that uranium, neptunium and plutonium can not properly be described as members of either a transition or rare-earth type series of elements.

The unusual characteristics of plutonium are emphasized by its behaviour when dissolved in thorium ; in this environment the plutonium atom apparently expands to a radius of 1.70A which is outside the range shown by the pure metal where the maximum radius is 1.65A. A radius of 1.70A for plutonium corresponds to a valency of 4 on Zachariasen's scheme. The radius of thorium is 1.79A and if plutonium had expanded to a greater extent the size factor for the solution could have been reduced even further but this would have meant a decrease of the valency below 4. Why the expansion stops at a valency 4 is not known—it may be due to the equality of the two valencies (expanded Pu and Th) or to an inability of plutonium to expand any further ; the latter possibility would be in agreement with the idea sometimes proposed that the basic valency of plutonium and the later elements is four, corresponding to a thoride series.

The observed alloying behaviour of plutonium is consistent with the well-known principle of size factor (S. F.) as judged by the extent of solid solubility and the occurrence of intermediate phases which are known to depend on the radius ratios of the components, e.g. ϵ -plutonium and γ -uranium exhibit continuous solubility—S.F. $\backsim$ 4% ; plutonium dissolves in thorium to a maximum of almost 50%-S. F. $\backsim$ 5% ; the solubility of plutonium in α -zirconium is remarkably large, ϵ plutonium and β-zirconium are probably continuous and there is a wide f.c.c. field-S.F. $\backsim$ 4% ; whereas for plutonium-iron the S. F. is $\backsim$ 20% and there is only slight solubility in some of the phases. In the case of plutonium-iron the radius ratio of 1.2 is close to the ideal value for the formation of Laves phases and in fact the $PuFe_2$ com-

pound belongs to this class of structures; the plutonium-manganese and plutonium-nickel systems have similar radius ratios and the Russian diagrams show PuM_2 phases in these systems. The plutonium-osmium system, also published by the Russians, is an intermediate case with a size factor close to the critical value for solubility of 15% and the modest solubility of osmium in ϵ-plutonium (6%) is in accord with this; in this system a Laves phase also appears and the radius ratio δ-Pu|Os is close to 1.2. Mardon and others[16] have discussed the occurrence of Laves phases in plutonium system in some detail.

Plutonium shows some similarity to uranium as far as the formation of certain chemical and metallic compounds are concerned, but in general its alloying behaviour is not similar. This is presumabely due to the different range of sizes and valencies shown by the pure metals which is magnified by the variable behaviour of plutonium on alloying.

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Discussions

Mr. L. M. Wyatt.. (*U.K.*) : Plutonium shows an increase of density with increase in temperature. I would like to know if there is any other metal that shows a similar behaviour.

Prof. Trombe. (*France*) : Yes. Plutonium is the metal showing an increase of density with increase in temperature. In the case of Gd and certain rare earths, there is a positive co-efficient of expansion along one axis and negative co-efficient along another, but the net change is in the direction of decreased density with rising temperature.

THE PHYSICAL METALLURGY OF THORIUM

*By M. K. Madhekar & M. K. Asundi**

The work on the physical metallurgy of thorium has been summarised under the following topics; structure and properties, mechanical properties, recrystallisation, metallography, deformation and texture, effect of impurities and alloys of thorium. Further, some practical problems associated with the physical metallurgy of thorium are discussed. Two appendices are attached giving some information necessary for the laboratory study of thorium.

Thorium occurs in nature in a much greater proportion than uranium and is a potential reactor fuel. From Indian point of view it has got an additional importance since we have the world's largest deposits of thorium.

Despite the large potentialities of thorium in the future power generation, its physical metallurgy and knowledge about the various possibilities of its practical use are still in a comparatively undeveloped stage than that of uranium. The reason for this is that thorium is a fertile and not fissile metal like U_{235} or Pu. It cannot be directly used in the reactor as a fuel, but must be converted into U_{233} before it can be used as a fuel. In this respect it is similar to U_{238}, which must be converted into Pu_{239} before it can be used as a fuel. The maximum permissible breeding ratios for thermal electrons originating from Pu_{239} and U_{233} are 1.03 and 1.25 respectively (16). Hence the cycle based on thorium as the fertile metal will be much more efficient in making more fuel than the consumption of uranium. This will no doubt lead to its intense study in the coming years.

Structure and Properties of Thorium

Atomic number of thorium is 90 and it belongs to the actinide series. According to the energy level diagram the 7s level is first filled and then the 6d and 5f levels are filled. The last element before the actinide series is radium, which has 6p and 7s shells completely filled. From actinium onwards 6d shell starts filling up. In thorium this shell contains two electrons. Since 6d and 5f energy levels are very closely spaced it looks probable that the two electrons are actually shared between these two levels, but recent work by Lehman (1) indicates that only the 6d shell is occupied by these two electrons. He has given a tentative curve for the density of states which is given in fig. 1. It shows that the density of states in 6d and 5f bands is 4 and 20 states per atom respectively and so if 5f band is partially filled it will mean relatively high electronic specific heat. But Lehman has obtained a straight line relationship between specific heat and tempera-

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ture. This shows that thorium has got negligible electronic specific heat and so does not contain any electrons in the 5f shell which has very high density of states. The 5f band is at least 1 eV above the Fermi level in thorium. On the other hand uranium has got nonlinear relationship between the specific heat and temperature, which indicates that in uranium 5f band is partially filled.

In most of its compounds thorium behaves like a tetravalent element but from the measurements of Hall's co-efficient it appears that the number of free electrons in solid state is somewhat less. The Hall coefficient of thorium is (2),-8.8 X 10^{-5} cc/coloumb; which gives about 2.4 electrons per atom.

Thorium is a naturally radioactive element with a half life of 1.389 10^{10} year and emits an alpha particle of 3.98 Mev. The radioactive series starting from thorium ends ultimately in $_{82}Pb^{208}$. Under the action of thermal neutrons thorium is transformed into U^{233} through an intermediate stage of Th^{233}. (U^{233} is a fissile element and so this reaction is used for breeding uranium from thorium).

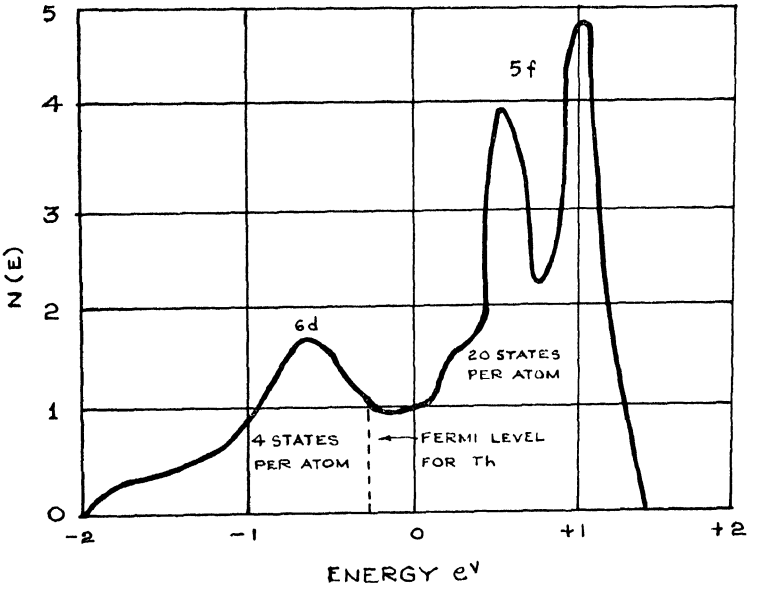

Fig. 1.—Qualitative Density of States for Thorium[1]

Allotropic modifications in thorium

Upto about 1400°C thorium has got face centered cubic structure. Thus during the whole of the useful range of temperatures thorium possesses a simple crystal structure. Due to this fact thorium does not behave erratically, like uranium, under the action of thermal cycling or radiation; and also it has got good machinability.

The two high temperature transformations in thorium one, the f.c.c. to b.c.c. transition at about 1400°C and second, the solid to liquid transition at about 1750°C, are very difficult to detect. In the solid liquid transition the heat evolution is so little that as much as 100 lb. ingots of Ames thorium solidify without showing any thermal arrest. Theoratically the heat of fusion of thorium has been calculated to be 4.6 kcal/mole[3] (3), but appears to be rather high in relation to the above observations.

Thorium is superconducting below a critical temperature lying between 1.4°K and 1.3°K (4). It is paramagnetic[5] (5) with a mass susceptibility of about 0.56 X 10^{-6} at 20°C. Below are given some of the important properties of thorium.

Table 1.—Properties of Thorium (7, 19).

Atomic number	..	90
Atomic weight	..	232.12
Crystal system	..	F.C.C. upto 1400°C, a=5.086± 0.0005 Å @ 25°C. B.C.C. 1400 to m.p. a=4.11± 0.01 Å @ 1400°C.
Elec. Resistivity	..	about 14 microohmcms.
Density	..	about 11.72 gms/cc.
Young's modulus	..	10.5 X 10^6 psi.
Shear modulus	..	4.0 X 10^6 psi.
Poisson's Ratio	..	0.27
Compressibility	..	16.4 $6m^2$/dyne.
Melting point	..	about 1750°C.
Boiling point	..	greater than 3000°C.
Heat of fusion		about 4.6 kcal/mole.
Heat of vaporisation		about 130 kcal/mole.
Specific heat in cal|mole|°C	..	6.59 at 99.3°C. 6.61 at 198.7°C.
Coefficient of Expansion	..	11.5 X 10^{-6} .. 30 to 100°C. 11.9 X 10^{-6} .. 100 to 500°C. 12.5 X 10^{-6} .. 500 to 1000°C.
Entropy	..	13.6 ±0.8 Cal/mole deg. C at 25°C.
Debye temperature	..	170°K.
Work Function	..	3.39 ev.
Thermal conductivity	..	0.090 cal/sec/cm/deg. at 100°C. 0.102 cal/sec/cm/deg. at 500°C.

Mechanical Properties of Thorium

The properties of thorium are dependent on its impurity content, especially the carbon content, and the difference in the properties of Ames and iodide thorium is now mainly attributed (6) to the higher carbon content of Ames thorium. Thus, whenever results for both

of these types were presented, those for iodide thorium have been given here.

Tensile strength: The tensile strength of thorium is extremely sensitive to the variation in carbon content, the variation in the strain rates, and the degree of work hardening. Fig. 2 shows the influence of strain rates on the tensile and yield strength of thorium (8). The

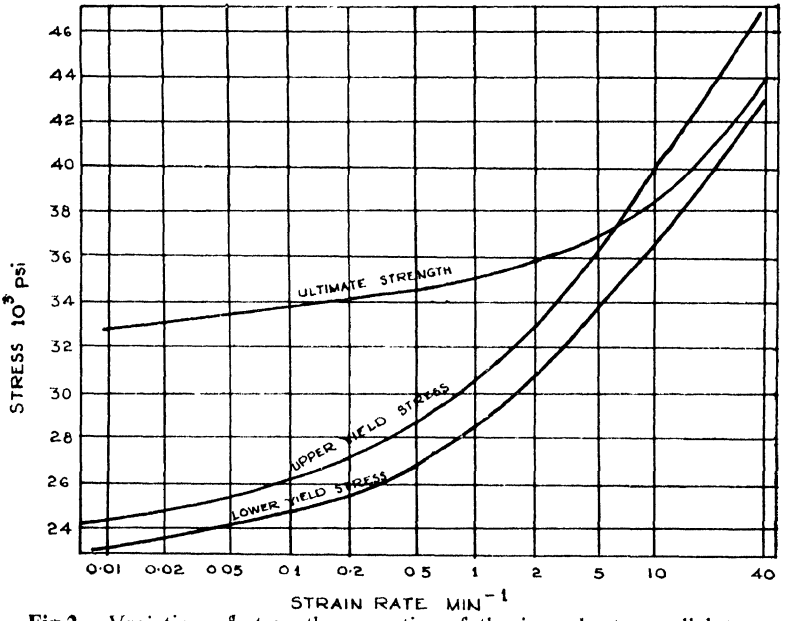

Fig.2.—Variation of strength properties of thorium sheet, parallel to rolling diretion, with strain rate (8).

tensile strength increases with the degree of work hardening and the reduction in area of upto 25% increases the tensile strength by about 30 to 40% and the yield strength by about 100%. Straining beyond 25% reduction in area does not further increase the strength. This indicates that work hardening is essentially complete before the reduction in area of about 25%. No appreciable difference in the strength in the directions parallel and perpendicular to the rolling direction have been detected.

Creep: Schowpe and others (9) have studied the creep properties of thorium in detail at temperatures 200°F (93.3°C), 400°F (204.4°C), and 600°F (315.5°C). For the creep properties at 400 and 600°F, the creep rates are influenced by some sort of an aging effect. For stresses greater than 15000 psi, creep resistance is greater at 400°F than at 200°F. For high stresses at room temperature, thorium may show high initial creep rate which becomes stable with time, at a small value.

Fatigue : Endurance limits for fatigue (8) of thorium are found to be approximately 12,000 psi for cast thorium, 15,000 psi for cold rolled thorium and 22,000 psi for hot rolled and annealed thorium. Fig. 3 shows the results of the axial load fatigue tests on thorium sheet specimens.

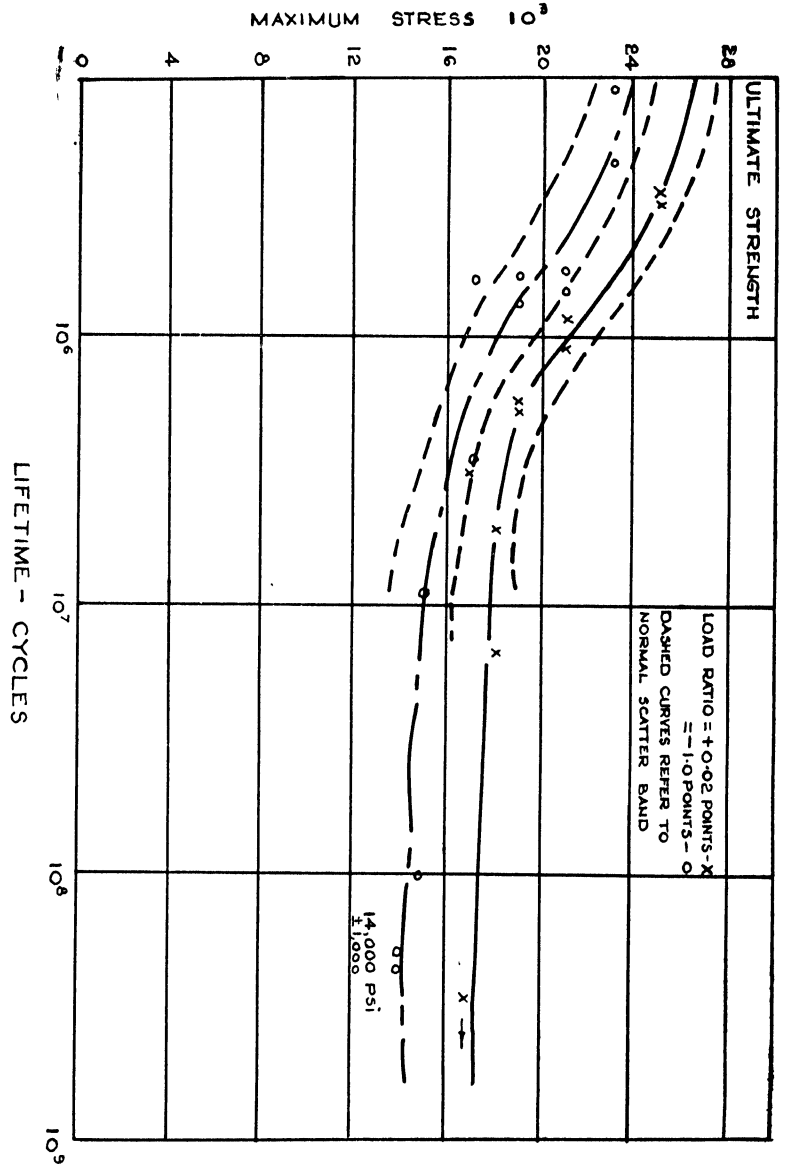

Fig. 3—Axial load fatigue test results on thorium sheet specimens (8)

Recrystallisation

Thorium is a very soft metal and allows severe cold working without intermediate annealing. Also since the solid state transition in thorium occurs at a very high temperature to be of any practical value, the major heating effect on thorium is recrystallisation.

Eckert and Boyle (10) have studied the recrystallisation behaviour of thorium by measuring hardness of thorium at different time intervals and temperatures. Two of the curves from their work are given here in fig. 4 and fig. 5. Figure 4 shows the effect of tem-

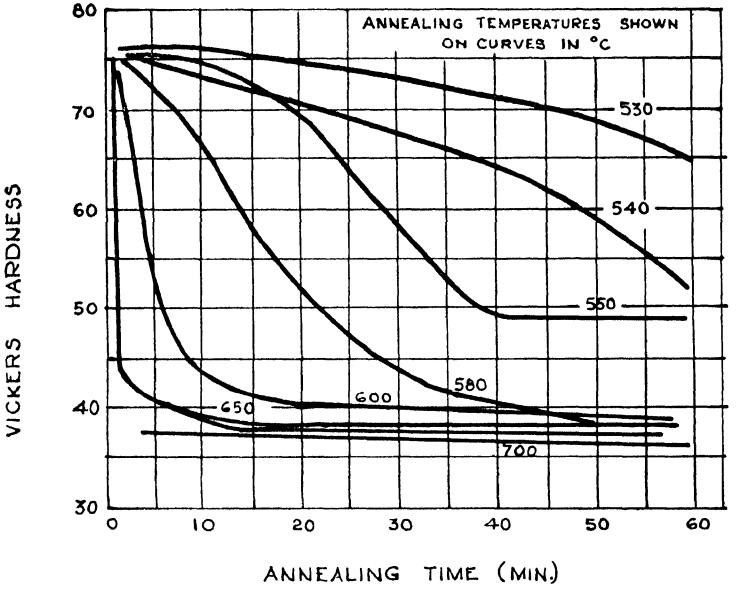

Fig. 4.—Isothermal recrystallization curves for iodide thorium[7] (Specimens cold worked to 80% R. A.)

perature on the recrystallisation behaviour after cold rolling to 30% R. A. Softening of thorium starts at about 500°C and with progressively higher temperatures recrystallisation is completed more and more rapidly. Figure 5 shows the influence of cold working on the recrystallisation of thorium. This shows that temperature of softening increases with decreasing amount of cold work.

Deformation and Texture

Comprehensive studies on the textures of cold rolled and extruded thorium have been carried out by Smallman (11) and Jetter and McHargue (12) respectively.

Smallman has also investigated the compression texture for thorium. It is similar to the compression texture of copper and consists of con-

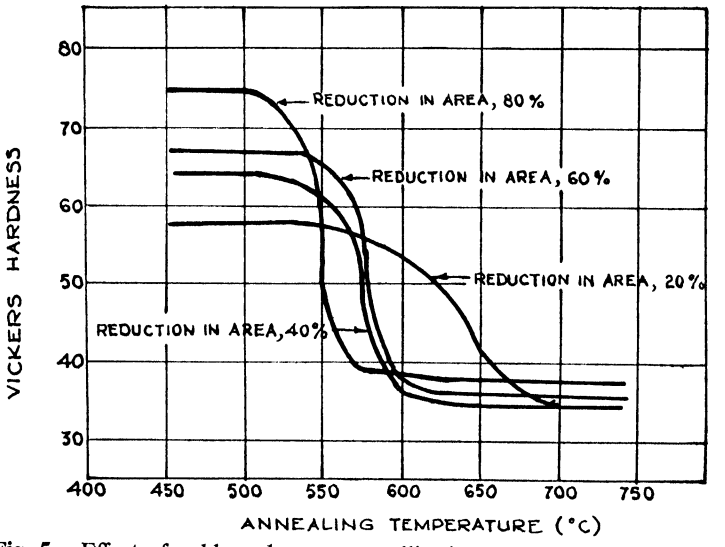

Fig. 5.—Effect of cold work on recrystallisation of iodide thorium (7). (Soaking time—1 hour)

centration round (110), absence round (111) and near absence round (100). It is shown in fig. 6.

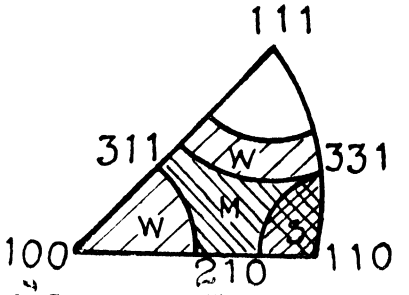

Figure 6—Compression rolling texture for thorium
W = Weak, M = Medium, S = Strong

For straight rolling the texture may be said to be roughly as four equivalent textures grouped around (123) [121]. These textures can be accounted for on the basis of slip on the octahedral plane in the direction of face diagonals.

Annealing texture for the rolled specimens is the usual (100) [001] cube texture and represents reorientation of the texture corresponding to 30° to 40° of rotation.

Jetter and McHargue have studied the extrusion, (@ 850°C) texture for thorium. At slow speeds the texture is [111] with some amount of [100]. It has been suggested that the [100] part of the texture is associated with recrystallisation of thorium. The relative

amount of [111] and [100] textures are proportional to the deformed and recrystallised portions of the specimens. Annealing at 750°C resulted in a duplex [115] + [235] or [013] + [4, 10, 13] texture.

For fast extrusion speeds the texture was predominantly [114]. Most probably this texture is associated with a high temperature process. The good agreement obtained between the yield stress and the calculated resolved shear stress indicates that in rods fabricated at these temperatures the texture markedly influences yield strength.

Metallography of Thorium

Thorium metal is obtained in sintered or cast form and does not respond satisfactorily to the usual metallographic techniques. At present several methods have been developed for obtaining microstructure of thorium. Some of these are given in Appendix II. These usually consist of combinations of mechanical polishing and electrolytic etching. No chemical etchant has so far been found for thorium.

The general procedure for the preparation of the sample consists of grinding the sample on silicon carbide papers either dry or wet, using lubricants like water, kerosene, wax etc. Some investigators prefer to avoid water, which tarnishes it. During grinding the soft metal is likely to pick up the abrasive and hence it must be ground very carefully. The usual difficulties associated with the polishing of soft metals are encountered.

Rough polishing is done on wheel with cloths of many types, from the ordinary brown cloth to microcloth; and using various types of abrasives ranging from ordinary rouge to diamond dust. Diamond paste is very useful in polishing thorium since it shortens the polishing time and gives a better surface.

Final polishing is done on soft clothes using Linde B alumina or fine diamond paste. For bright polished surfaces 10% solution of oxalic acid is used.

After this final polishing, the specimen is quite suitable for microscopic examination of the inclusions etc. If a study of grain size and structure is to be undertaken the sample is either electropolished or electroetched. Mere electropolishing may be sufficient to reveal the grain structure.

The appendix II gives a number of electrolytes to be used for polishing and etching purposes. It may be noted that almost all the solutions attack the inclusions and develop pits on the surface. Thus, to study the inclusions it is necessary to study the specimen in the as polished state.

Vacuum cathodic etching has been tried by Carlson (15) and his work on thorium shows that this method holds promise as an alternative to the normal methods. But the method is still not developed and standardised.

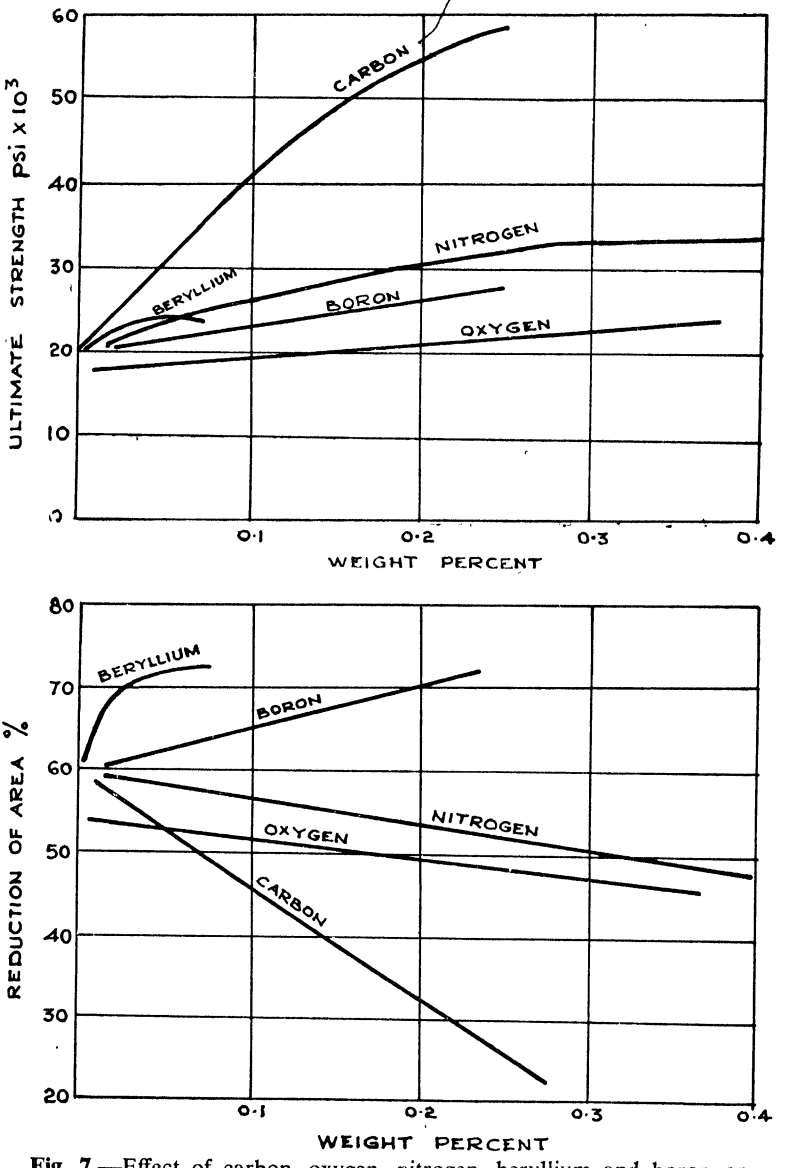

Fig. 7.—Effect of carbon, oxygen, nitrogen, beryllium and boron on the strength and ductility of iodide thorium[6]

Effect of Impurities on Thorium

The main impurity that considerably affects the properties of thorium is carbon. Goldhoff and others (6) have studied the effect of C, B, Be and N on thorium. Effect of these elements on the strength and ductility of thorium are shown in fig. 7. From these cur-

ves it can be seen that carbon is the most important impurity in thorium. Carbon has also got age hardening effect on thorium and solubility of carbon in thorium is given below for various temperatures (13).

Room temp.	0.35%
800°C	0.43%
1018°C	0.57%
1215°C	0.91%

Fig. 8 shows influence of carbon on the recrystallisation of thorium.

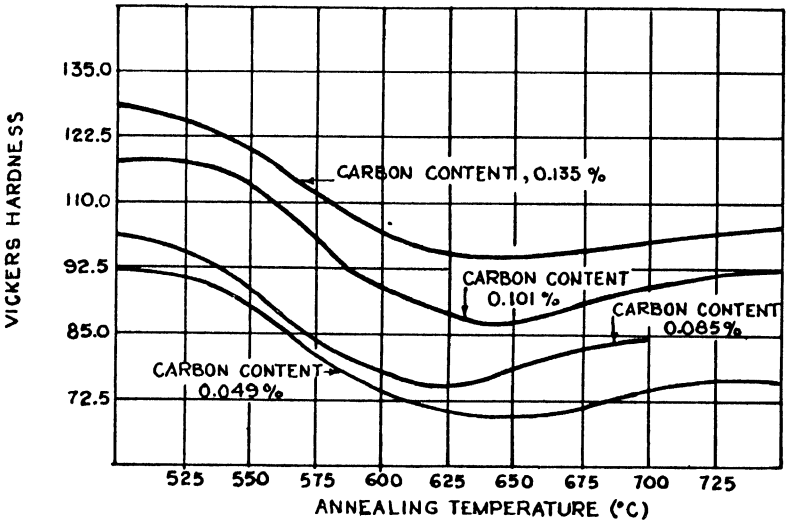

Fig. 8.—Effect of carbon on recrystallisation of thorium (10) Annealing time one hour. The specimens were made from ingots reduced 35% in area and homogenised for 12 hours at 1275°C

It is of interest to note that the study of combination of the effect of alloying with carbon, age hardening and cold working has shown that a 0.11% carbon alloy, with proper degree of age hardening and cold working, can give double yield strength and tensile strength, maintaining adequate ductility(6).

Nitrogen has also got age hardening effect, but it is of a much smaller magnitude. Indium and Uranium increase the hardness of thorium whereas the addition of titanium, niobium and molybdenum actually soften it. This is believed to be due to the scavenging action of these elements on the carbon in thorium. Alloying thorium with two elements like C and In or C and U gives results which are much better than the simple additive effect will show (6).

Alloys of Thorium

The atomic diameter of thorium is 3.59 Å and only a few elements have got diameters within the favourable range to form extensive solid solutions. Table 2 shows the percent difference in the atomic diameters of various elements and thorium.

Table 2.—Percent difference in the Atomic diameters of various elements and thorium

Element	$\frac{DTh-Dx}{Drh} \times 100\%$	Element	$\frac{DTh-Dx}{Drh} \times 100\%$
Bi ...	—1.4	Ti ...	18.4
Ce* ...	—1.4	Au ...	19.8
La* ...	—4.2	Ag ...	19.8
Tl ...	4.7	W ...	21.4
Pb ...	8.3	Al ...	22.0
Na ...	6.7	Mo ...	22.0
Sb ...	10.0	Ge ...	22.2
Mg ...	10.9	Pt ...	22.8
Zr* ...	11.1	Zn ...	23.3
Hf* ...	11.7	Pd ...	23.6
Sn ...	12.0	V ...	24.4
In ...	12.5	Cr ...	27.8
Li ...	12.8	Cu ...	29.0
Hg ...	13.7	Co ...	30.4
Nb ...	15.3	Fe ...	30.4
Ta ...	15.3	Ni ...	30.6
Cd ...	15.3	K ...	32.7
		Si ...	34.8

* Denotes that the element has got extensive solid solubility in thorium. This line denotes the line beyond which the atomic diameters are unfavourable for forming extensive solid solutions.

According to the table 2, the elements Mg, Zr, Hf, Ce, La, Pb, Ta, Bi, Sb etc., have got favourable atomic size factors, but thorium is extremely electropositive and extensive solid solutions are formed only

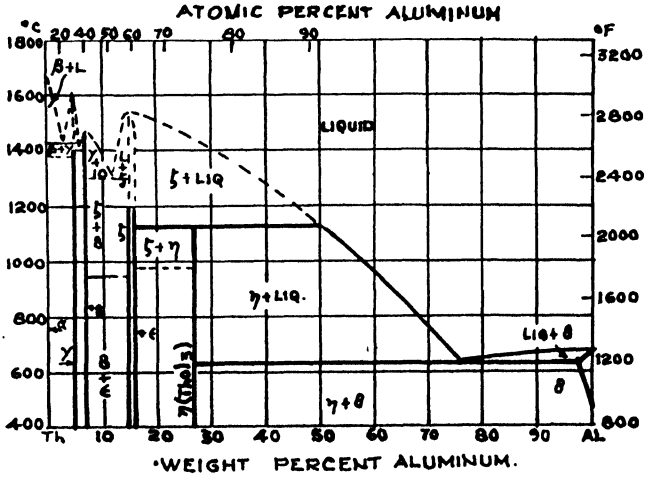

Fig. 9.—Thorium-Aluminium System

with Ce, Hf, La and Zr. It forms simple eutectic systems with the elements Cr, Nb, Ti, W, U and V and with the rest of the elements it

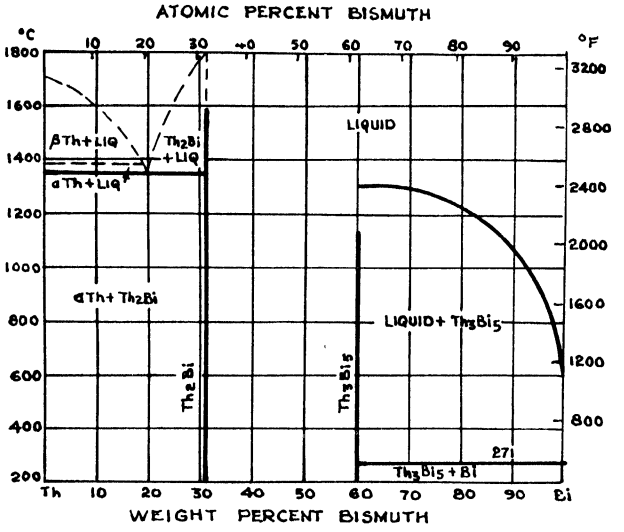

Fig. 10.—Thorium-bismuth system

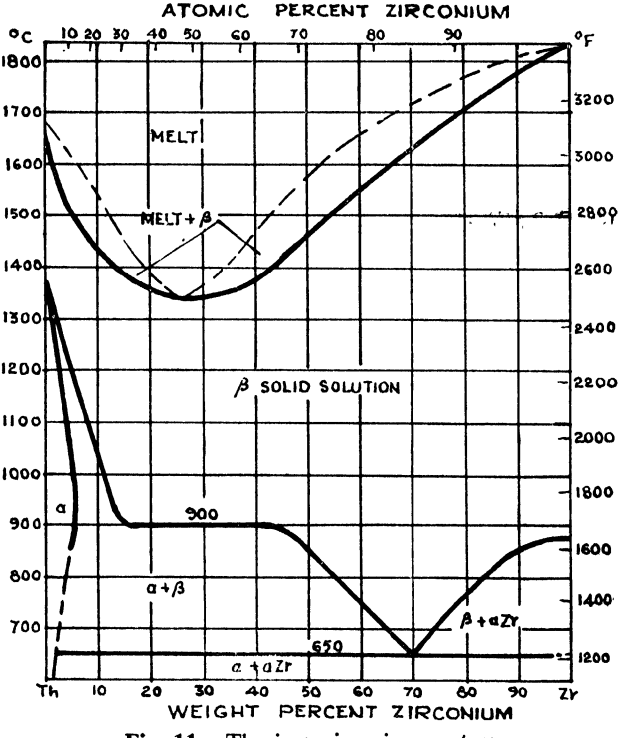

Fig. 11.—Thorium zirconium system

forms complex systems containing many intermetallic compounds. Figures 9 to 18 show the systems (3, 7) Th-Al, Th-Bi, Th-C, Th-Cr, Th-Ni, Th-Nb, Th-Ti, Th-U, Th-V and Th-Zr.

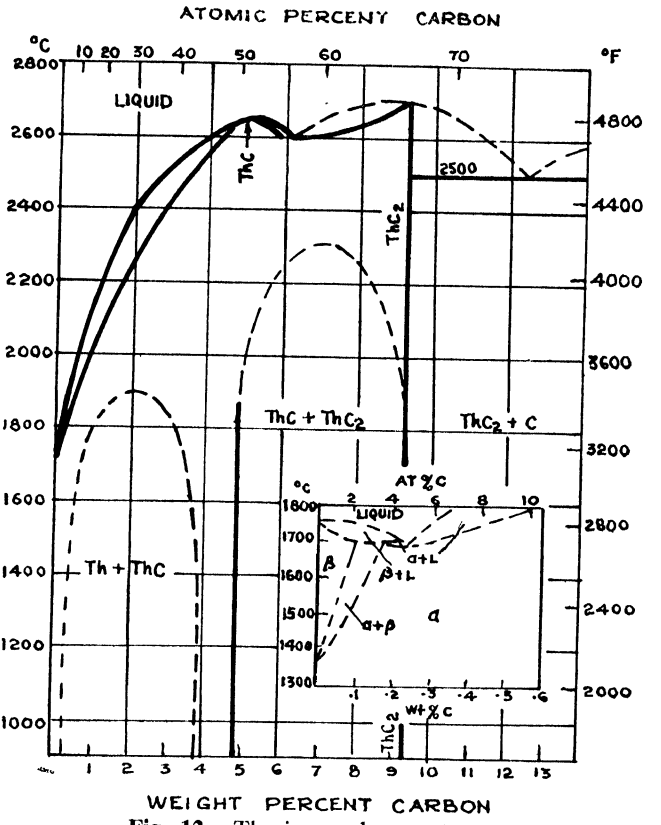

Fig. 12.—Thorium-carbon system

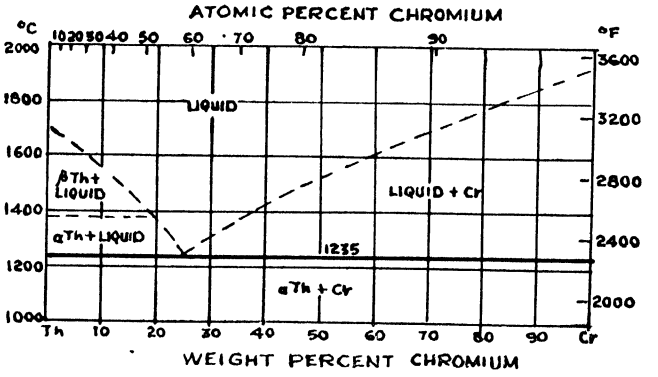

Fig. 13.—Thorium-chromium system

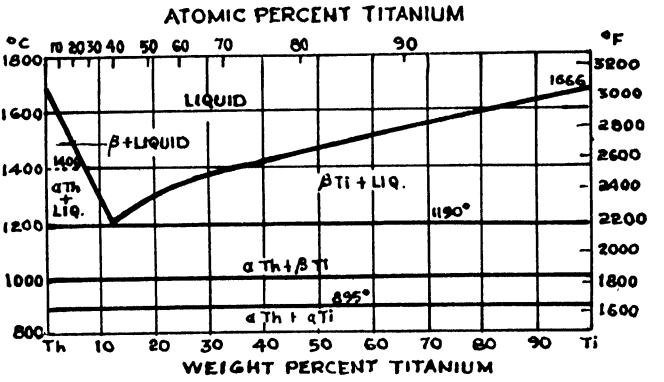

Fig. 14.—Thorium-titanium system

The alloys of thorium with uranium and bismuth are of particular interest from the point of view of nuclear energy and will be discussed to some extent in the next session.

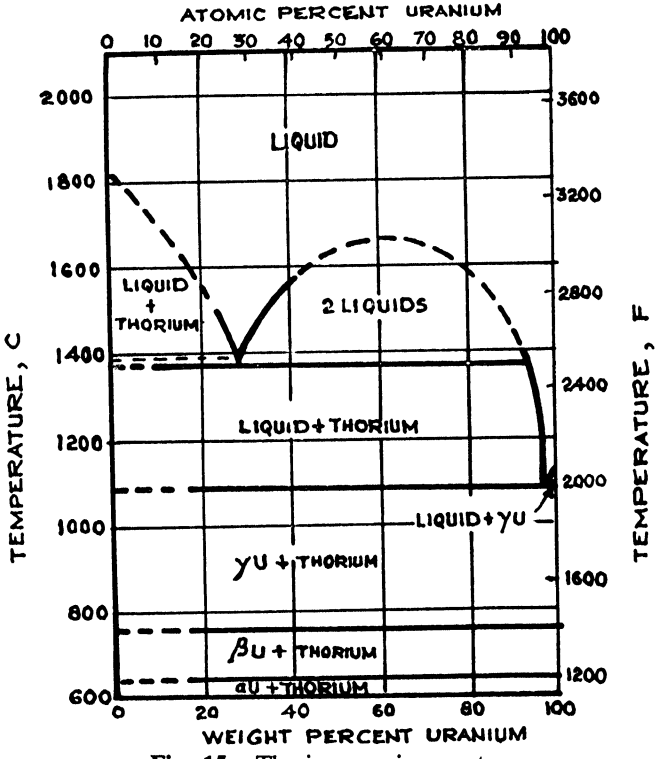

Fig. 15.—Thorium-uranium system

In this place it will be of some interest to note that thorium can be used as an alloying element with magnesium to increase its creep

resistance (14). Thorium increases the strength and ductility of rolled sheets of the alloy. The creep resistance of the Mg-Th alloys at 500° and 600°F is the highest yet obtained in any magnesium alloy. Addition of 3% Ce to 3.6 and 10% Th alloy increases the yield strength of the alloy significantly upto the temperature of 400°F.

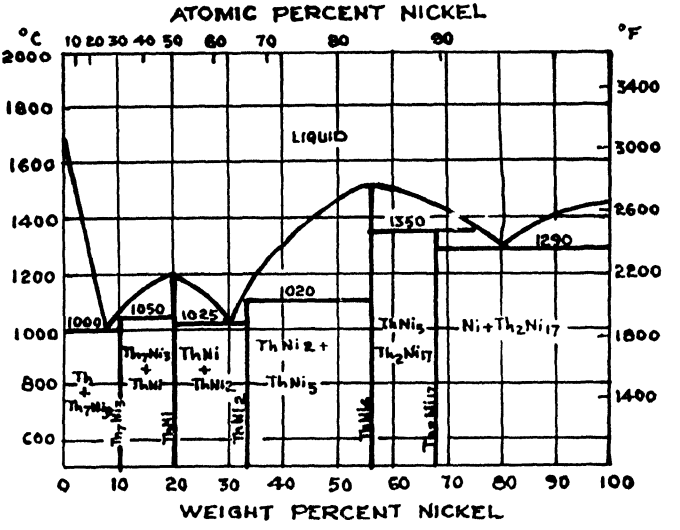

Fig. 16.—Thorium-nickel system

Some practical aspects of the physical metallurgy of Thorium

The main problems arise from the use of thorium as a breeding material in reactors. This involves placing thorium near the reactor

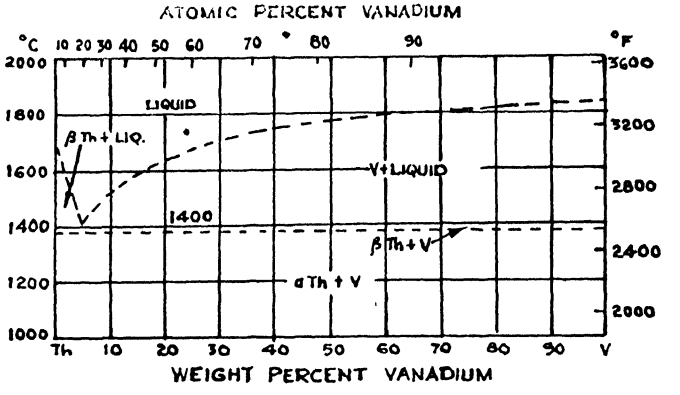

Fig. 17.—Thorium-vanadium system

elements which are either made of U_{233} or U_{235} or circulating it through the reactor core by means of a liquid medium, usually bismuth. This involves.

1. mixing of Th with U in the fuel rod itself (16)

or 2. placing alternate layers of U and Th rods (16)

or 3. making a slurry of thorium in liquid bismuth (17, 20) which can be circulated through the reactor core.

These, in turn, give rise to the following physical metallurgical problems.

1. Behaviour of uranium-thorium alloys at the operating temperature for the reactors.

2. Cladding of thorium with various elements, notably zirconium.

3. Behaviour of the intermetallic compound Th_3Bi_5 in liquid bismuth.

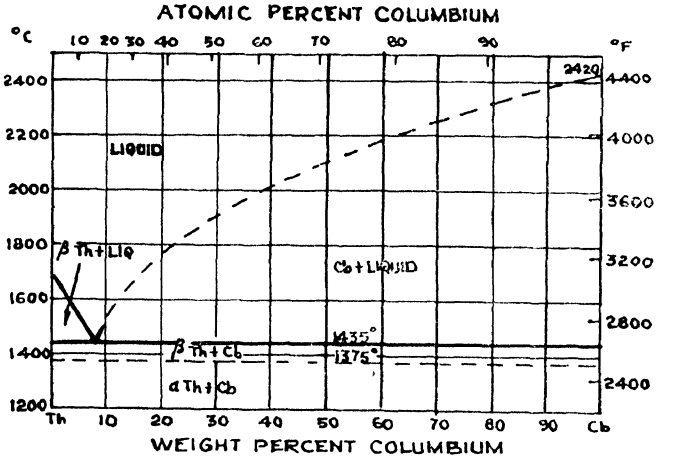

Fig. 18.—Thorium-niobium system

Uranium and thorium are completely insoluble in each other in the solid state and form a eutectic and a monotectic. The diagram for the system is given in fig. 17. It shows that for the temperatures at which the reactor operates we get simple mixture of uranium and thorium.

Cladding of thorium and its alloying with various metals to increase its strength are still problems in its initial stage of development.

Thorium is soluble in bismuth to only a very limited extent and when it is added to liquid bismuth, particles of thorium bismuthate (Th_3Bi_5) are formed (17). These are precipitated in the form of platelets and this shape is undesirable in the slurry, since the platelets are liable to

block the passage of the moving slurry. Thus, it is necessary to obtain these particles in an equiaxed shape. This has been achieved in various ways, some of which are (20), 1. heating in the form of lumps in contact with liquid bismuth at temperatures below the liquidus but above 420°C., 2. ultrasonic method, 3. electrolysis, etc.

Conclusion

Metallurgical problems of thorium are comparatively simple than those of uranium, due mainly to its simple crystal structure. But further extensive experimentation is necessary before it occupies its proper place in the field of nuclear metallurgy. The main obstacles in the study of thorium are its very high melting point, low corrosion resistance and considerable radiation hazards associated with it. Nevertheless these obstacles can be readily surmounted and considerable advance in the understanding of its structure, properties and alloys is expected in the near future.

Appendix I.

Preparation of Sintered Specimens for laboratory studies : Since the melting point of thorium is very high and since it is difficult to produce alloys of exact composition by casting, technique of powder metallurgy has been extensively used for preparing thorium specimens. If thorium powder is compacted, sintered, cold worked and again sintered we get material of almost theoretical density. Optimum conditions for obtaining such specimens are given by Smith and Honeycombe (18) as follows : (1) Pressing at 22 tons/sq. in. (2) Sintering at 1300°C for 2 hours. Density obtained about 11.0 gms/cc. (3) Cold rolling to 50% reduction in area. (4) Resintering at 1300°C for 1 to 2 hours. Density obtained 11.60 to 11.66 gms/cc. Density of solid thorium is about 11.7 gms/cc. The main impurity in such specimens is thoria.

Appendix II

Some methods for Metallographic Examination of Thorium.

1. *Method of Baumrucker at Argonne National Laboratory* :

Grinding : Papers 180, 240 and 400 grit on wheels. water lubricant. Hand grinding on 3/0 and 4/0 kerosene lubricant. Fine grinding on Metcloth; abrasive 600 mesh SiC, kerosene lubricant.

Polishing : Selvyt cloth using 14μ, 6μ & 1μ diamond as abrasive. Final polishing on Selvyt using Linde B abrasive suspension in ethylene glycol.

Electrolyte : Phosphoric acid 5% vol., Sulphuric acid 10-15% Vol. Nitric acid 15% Vol., Ethylene Glycol 70-65% Vol. 75 mA/sq. cm., 30 seconds, 42-45°C.

Remarks : Care must be exercised during grinding and polishing. The metal picks up abrasives. Thorough cleaning between successive laps. The solution must be used within two hours. It decomposes if kept for longer duration.

2. *Method of Peterson at Ames Laboratory.*

Grinding : 320, 400 and 500 and 600 grit SiC. No lubricant. Ground for a short duration on cotton broadcloth using 400 grit carborundum suspension in soap solution.

Polishing : On Forstman's cloth using a suspension of 600 grit SiC in soap solution.

Etching : Electrolyte. Nitric acid 1 part and water 7 parts. Made 0.003 molar in sodium fluosilicate. 50-150 mA/sq. cm., 20-60 seconds at room temperature.

Remarks : Bath must be agitated during etching. Inclusions are severaly attacked.

3. *Method of Pohl at Knolls Atomic Power Laboratory.*

Grinding : Upto 600 grit SiC. Kerosene lubricant.

Polishing : For a short time on fine grade cotton broad cloth charged with a slurry of Precisionite (0.3μ), distilled water and a few drops of liquid soap.

Electropolishing : I. Glacial acetic acid 300 cc. perchloric acid 25 cc. Water 5 cc. 12-30 volts, 6 to 30 seconds at 15°C. II. Acetic acid 100 cc. and phosphoric acid 90 cc. 17.5 volts, 15 to 30 minutes.

Remarks : 1. Bath must be gently agitated. This gives both polishing and etching. II. This solution polishes the surface bright and also retains the inclusions. Etching may be done at 4.5 volts, but it removes all the inclusions.

4. *Method of Roth at MIT*:

Grinding : Hand grinding on 320 and 600 grit SiC papers, Used papers give better results. Lubricants used kerosene and wax solution.

Polishing : On broadcloth and later on wool covered wheel using Linde A suspension in 10% oxalic acid. Liquid soap used during polishing.

Electropolishing : In 2 litre solution of ethyl alcohol 15 parts and perchloric acid 1 part, for 15 to 45 seconds at 35 to 40 volts.

Remarks : Reveals grain size but inclusions are removed during polishing.

5. *Method of Cain at Westinghouse Atomic Power Division* :

Grinding : On 240 grit SiC belts, O emery paper and 600 grit SiC wet wax lap.

Polishing. Best polishing was obtained on Microcloth using 0.1μ Linde B Sapphire dust.

Electrolytic etching : A. for bright field.—Potassium ferricynide 7 cc. of 10% solution, conc. acetic acid 1 cc., sodium picrate 2 cc. of 5% solution distilled water 90 cc. 18 to 20 Amp/sq. in. for 5 to 30 seconds at 65 to 70°F. Metallographic structures are revealed clearly. The electrolytes are non-explosive. After etching the specimen must be washed first in conc. acetic acid and then in warm water.

B. for polarised light—Potassium ferricynide 7 cc. of 10% solution and sodium borate 3 cc. of 5% solution, at 8 to 10 Amp/sq. in., 10 to 20 sec. and 65 to 70°F. After etching the specimen must be washed in warm water.

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The phase diagrams given (figs. 9 to 18) have been reproduced from the references 3 and 7.

TECHNOLOGY AND APPLICATIONS OF THE RARE METAL OXIDES AND CARBIDES

*By V. K. Moorthy**

Power reactors are now an accomplished fact, only the initial cost and other economic considerations still standing in the way of their[24] more wide-spread application. So long as the heat energy released in the reactor is to be converted into electrical energy for ultimate use, the efficiency of the unit would increase with the operating temperature of the reactor, which is limited by the materials of construction. The development of reactors operating at high temperatures depends mainly on the availability of suitable materials both for the core and the structural components of the reactors.

The nuclear properties of interest for reactor technology are dependent only on the structure of the nucleus and are not materially altered by the chemical combination in which the nucleus occures, e.g. for a fuel element, the fissile nucleii can be introduced with equal facility either as metal, oxide, carbide or any other compound of the parent metal. The physical properties of the material, which are of interest for reactor engineering, are however profroundly influenced by the chemical composition of the material. Oxides, carbides and some other compounds of the metal are more refractory than the metals and can be used in reactors operating at high temperatures. It would however, be necessary to make modifications in the reactor designs to suit the other properties of the available materials.

In addition to their refractoriness ceramic materials exhibit certain desirable properties for reactor applications, such as creep strength, corrosion resistance and in some cases resistance to radiation damage to a greater degree compared to the metals. However, they are brittle, have poor impact strength, a low thermal conductivity and low thermal shock resistance. The effect of the undesirable properties, can to some extent be minimised by developing suitable cermets, which give properties intermediate between those of ceramic materials and metals. The scope for developing ceramic materials and cermets with the desired high temperature properties is practically unlimited.

The present paper deals with the available information on oxides and carbides of the more important metals used in nuclear applications.

Special properties of refractories for Nuclear Energy applications

The refractory products, either for use in melting nuclear pure metals or for use as reactor components differ from conventional clay

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ceramics in the following respects :—(1) They have to be of a high purity; particular care should be taken to keep the impurities which influence the nuclear properties to a very low level (a maximum of few parts per million). (2) As the oxides or carbides contain fewer atoms of the material of interest in nuclear application than the metals, attempts have to be made to get maximum density. This would also be necessary to improve some physical properties such as corrosion resistance. (3) The melting points of these materials are very high. As a consequence the temperatures required for sintering them are much higher than the ones used for conventional ceramics and refractories. (4) The materials do not have the natural plasticity.

Fabricating techniques

General : In view of the above considerations, the fabrication techniques for the refractories for nuclear applications need special attention, though the methods used are essentially modifications of the conventional ceramic forming processes; the principal methods[1,2] used in the formation of shapes are (1) slip casting[3], (2) extrusion, (3) tamping, (4) dry pressing, (5) isostatic or hydrostatic pressing[4,5] and (6) hot pressing[6,7]. The choice of the method depends on the shape and size of the article required and the desired end properties. Slip casting is suited for the production of thin walled ware (crucibles, boats etc) extrusion for rods and tubes and the pressing techniques where high density is essential and the length to diameter ratio of the sample is not high. Isostatic pressing and hot pressing, which, though known, were little developed, are found to be very valuable for this application.

Whichever of the forming techniques is adopted the material is required in a very finely ground state (particle size 10 microns and less) in all cases to promote compaction and sinterability. In the slip casting and extrusion processes this is all the more necessary to develop a certain degree of plasticity. Use of either fused or a high temperature calcined material is always preferred to give a high density and to prevent excessive shrinkage during sintering. As already pointed out, purity is a very important consideration in these products. Hence care has to be taken to prevent contamination during the processing of the materials especially during the preparation of fine particles. One method suggested is that the fused or calcined material be crushed in ball mills having a lining and with crushing media of noncontaminating materials, such as the metals or the fused oxide of the material being crushed e.g. using a pure alumina lined mill and fused alumina balls for grinding alumina, rubber lined mills using zirconium metal or fused zirconia balls for grinding zirconia etc.

Conventional ceramic techniques : Some information on the application of the different forming methods is available in the literature. Slip casting techniques[3], using plster of paris moulds, were successfully used in the production of alumina, beryllia, thoria, zirconia and zircon bodies from aqueous slips. Either strongly acidic or strongly alkaline

slips have been used in most cases; neutral aqueous slips find little application. Non-aqueous slips can be used in cases, where aqueous slips are not suitable for any reason. Calcia and magnesia, which are prone to hydration in aqueous slips, have been successfully cast from 'absolute alcohol' slips.

Extrusion of the special refractory bodies present certain problems not ordinarily faced with clay ceramics, such as choice of a plasticiser to impart the necessary workability, control of the particle size in the body and die and press designs for operating at high presures.

Tamping presents fewer problems compared to either extrusion or slip-casting. The required workability in the body is obtained by addition of gelatinous substances, such as starch paste or cellulose derivatives, which burn off during firing. In the case of certain oxides like Mgo, ThO_2 or BeO, workable bodies can be obtained by wetting the material with the respective chloride solutions. The hydrated oxy-chloride formed, which decomposes during firing, provides the bond during the forming and in the green state.

Techniques of dry pressing[6] of the powders are essentially the same as for the clay ceramics. Special attention however, has to be given to the particulate composition of the body and the choice of suitable lubricants or plasticisers. As considerable pressures, in some cases as high as 100,000 p.s.i. are applied, special attention has to be paid to the design of the dies.

The shapes formed by any of the above techniques have to be sintered generally at temperatures between 1800°-2000°C. This can be done either in gas fired, carbon resistance or induction furnaces. The usual precautions of controlling the heating rate, the atmosphere in the furnace and the time and the temperature to develop the desired degree of sintering have to the taken. In certain cases, it may be desirable to prefire the ware at a lower temperature (compare biscuit firing, in clay ware) to make them amenable to machining.

Special Techniques: (a) *Isostatic pressing*: Isostatic pressing[4,5] has been little used for conventional ceramics. Normal dry pressing cannot be used to produce articles having a shape of any complexity. Even simple crucible shapes cannot be made having a uniform density throughout. The isostatic pressing combines the ease achieved by straight die pressing with great flexibility to produce shapes of uniform density throughout the body.

In this method, the powder with the necessary binding material such as methyl methacrylate, is enclosed in an elastic former. The former should have the elastic properties, (which enable it to spring away from the body after the pressure is released) impermeability to liquid, the ability to form into a variety of shapes and sufficient hardness to prevent the refractory particles from becoming embedded into its sur-

face. Polyvinyl chloride has been found satisfactory for this application.

The sample enclosed in the former is placed in a hydrostatic chamber and pressure gradually applied. For hollow bodies, such as crucible shapes and tubular forms, the pressing can be either from outside in or inside out or the pressure can be applied in both the directions. The shapes formed are sintered at the desired temperatures by the usual methods mentioned earlier.

Important advantages of this technique are :

(1) The ware produced has a high green strength and can be machined before firing.

(2) The ware, its surface in particular, is uniformly dense.

(3) The ware does not warp during the sintering.

(4) Pieces of somewhat complicated shape can be made, with the above properties.

(*b*) *Hot pressing* : Hot pressing[7] of refractory materiasls is a relatively new technique, whose application has been limited to a few materials. The advantages of hot pressing are (1) dense and accurately shaped ware can be formed and sintered in one operation at a temperature lower than the usual sintering temperature of the material, (2) ceramic bodies can be fabricated in much shorter time than by conventional methods and (3) complicated shapes can be made, without much difficulty.

In this techniques the material is heated in a suitable die to the required temperature and the necessary pressure applied and held for the required duration. Induction heating is widely used for hot pressing because of the ease with which high temperatures can be attained rapidly. As the temperatures required for sintering refractories are too high for other die materials, graphite has become the universal die material for hot pressing applications. It has the advantage that it is a good electrical conductor and can act as the core in induction heating. The low strength of graphite limits the applied pressure to about 4000 p.s.i. Due to the intrinsic limitations, the maximum size of specimen that can be made by this method is about 4 inches diameter.

The conditions for hot pressing are profoundly influenced by the nature of the powder used and have to be determined for each material. The two significant factors influencing the sintering rate of the material and the final density obtained are (1) the method of preparation of tthe material and (2) the particle size. These have been discussed in the case of UO_2 and ThO_2 powders by Murray[4] et al.

Hot pressing has been widely used for the production of dense shapes from very refractory materials. It is the most important technique for the development and production of cermets.

Applications of Oxides and Carbides in Nuclear Technology

In Nuclear Metallurgy : (a) *Crucible material* : Ever since the nuclear energy programmes were started, the need for special refractories was felt. Pure refractories were required for melting the hitherto little known metals. Refractories of practically no porosity were required for use in the vacuum fusion furnaces and for laboratory applications like zone melting. Magnesium oxide[8] has been used for making crucibles and as a mould material for melting and casting of uranium and its alloys. For the production of extra pure uranium for experimental purposes, calcia[8] crucibles have been preferred as this results in less silica pick-up in the metal. Thoria has been preferred for melting thorium metal and thorium—uranium alloys. Alumina has been used for boats, crucibles and refractory tubes in laboratory furnaces and alumina blocks find application in hotpressing equipment. Beryllia exhibits a high thermal conductivity and a great corrosion resistance; it finds application where these properties are made use of e.g. in heat transfer systems using liquid metals, in zone melting of uranium etc. Numerous other applications of the ceramic crucible materials are listed in the crucible hand book[9].

(b) *Ceramic coatings* : Ceramic coatings[10] for graphite molds and crucibles used for melting and casting of metals like uranium were desired to (1) minimize the contamination due to carbide formation and (2) aid in an easy release of the ingot from the mold. Magnesia, alumina, high alumina compositions and magnesium zirconates have been applied on graphite ware used in the vacuum casting of uranium and its alloys. The use of the coatings not only results in cleaner and purer ingots but also increases the life of the graphite crucibles and molds.

In reactor technology : (a) *General considerations* : The development of power reactors operating at high temperatures, is limited by the availability of suitable materials for the components. Ceramics and cermets are most suited to fulfil this requirement and it is in the aspect, as components of the reactor, that ceramics plays a vital role in future developments of power reactors[23].

Ceramic components find application in reactors,[10, 11] where (1) their high temperature properties are desirable (2) their nuclear properties are desirable and (3) the corrosion resistance is greater compared to metals. In some cases they may be preferred at even lower temperature, if the metal shows an undesirable phase transformation in the operating temperature range.

In general, ceramic matrials are more refractory than the metals,

have adequate strength at elevated temperatures, have a better corrosion resistance than metals, more so at elevated temperatures and have sufficient degree of other properties such as corrosion and erosion resistance. Their thermal shock resistance, however, is very low compared to that of metals. The nature of radiation damage in ceramic materials is still not clearly understood but it is believed that it would be lower at elevated temperatures.[12,23]. Available information on urania, indicate that radiation damage in ceramic materials is not likely to be a very serious problem.

The general properties mentioned above indicate that ceramic materials can be adapted for use in the reactor core. The limited information available so far on the application of these materials as reactor components is discussed below.

(b) *Fuel elements* : 1. *Oxides* : [13, 14, 15, 22]. The following table[16] of the melting points of metals and oxides of uranium and thorium shows that the oxide is more refractory than the metal in both the cases.

	Uranium	Uranium Dioxide UO_2	Thorium Th	Thoria ThO_2
Melting point °C	1132	2800	1827	3200
Thermal (Conductivity C.G.S. Units).	0.071	0.023	0.090	0.0245
Density gms/cc	18.8	10.97	11.3	10.15

Of the compounds of uranium the dioxide has received considerable attention because of its refractory nature and its resistance to aqueous corrosion. Unlike the metal it is safe to use UO_2 in high pressure water reactors. UO_2 pellets clad in zircalloy-2 are to be used in the Shippingport pressurised Water Reactor.

The technology of UO_2[4] has progressed considerably in the last few years. In bulk uranium dioxide can be fabricated by any of the conventional methods. Sintering is usually done between 1500-2000°C in vacuum, inert atmosphere or hydrogen to prevent the UO_2-U_3O_8-UO_2 change which involves a volume change of about 50%. Isostatic pressing at about 40,000 p.s.i. and firing at 1750°C for two hours in hydrogen atmosphere yielded samples of about 90% of the theoretical density. Simple shapes can also be made by hot pressing at 1500-2000°C at a pressure of a few thousand pounds per square inch.

Production of dense urania shapes[13] is aided by the following: (1) the use of dense grains (2) use of fine grains to promote sintering and (3) by the use of additives to lower the sintering temperatures. Dense particles can be made either by fusion (carbon arc) or by sintering at temperatures between 1800 to 2000°C. The use of the fused grains is however limited by the poor efficiency and the hazards involved in the fusion process. To study the possibility of reducing the sintering

temperatures, compositions with MgO, Al_2O_3, BeO ThO_2, and UO_2 have been studied [17]. The UO_2—ThO_2 systems proved eminently suitable. In this system samples containing upto 25% UO_2 could be made by using U_3O_8 and ThO_2 and firing upto 1850°C in air; sintering aids such as CaO, MgO and CaF_2 aided in densification.

Thoria[18] is of potential interest as a breeder material. Thoria is stable in air at all temperatures and presents no special problems in the fabrication. Sintering and densification are dependent on the preparation of the powder. Additives to lower the sintering temperature have been studied and CaO has been found to be helpful.

Carbides : The properties of the mono-carbides of uranium and thorium are given below[16] :—

	UC	ThC
Structure	Cubic	Cubic
Melting point °C	2250	2625
Density gms/cc	13.63	10.65

The use of the mono-carbides is preferred because they are relatively richer in metal content and because of their stability upto their melting points.

The high thermal conductivity of uranium carbide (UC) closer to that of the metal than the oxide) and its volume stability up to the melting point, make it a promising material for use as fuel elements.

Shapes of uranium carbide can be fabricated either by dry pressing or isostatic pressing and sintering at about 2000°C or by hot pressing at a pressure of about one ton per square inch at a suitable temperature between 1600—1900°C. Uranium carbide can be used advantageously as a base in cermets e.g. UC|U, which might have more desirable properties, e.g. UC|U cermet exhibits all the desirable properties of UC and in addition possess a high density.

Service considerations : The service considerations of the materials are more stringent in the fuel elements than in other components of the reactor. Hence the limitations of ceramic materials for this application are considered. Because of the low thermal conductivity there is a tendency for the build up of core temperature in the ceramic fuel elements. In reactors operating at high power using uranium dioxide as the fuel elements, Handwerk and Noland[19] have reported core temperature between 1060°C and 3900°C in ¼″ diameter elements. This is undesirable in view of the low thermal shock resistance of the material.

The low thermal shock resistance[16,23] of the bulk solid may be artificially improved by (1) reducing the size of the unit composing the fuel element or (2) using a fuel element consisting of a dispersion of small fissile particles in another phase. The latter is feasible if enriched uranium is used and has two obvious merits, viz.

1. because of the reduced size of the fuel element the thermal shock resistance of the fuel material is no longer a problem.

2. if the dispersion is dilute enough, as it may be with enriched uranium, irradiation damage due to fission fragments is restricted to a small volume round each fissile particle.

The dispersed type of element could consist[16] of a dispersion of the fissile (or fissile/fertile material, if breeding is also being considered) in the moderator or of a cermet of ceramic fuel in a metal matrix. In the first case the dispersion of the appropriate carbides, in graphite is possible or of the appropriate oxides in beryllia. In the case of a cermet a system as UO_2-Fe or UC-Zr could be considered. The cermet system may be extended to include a completely fissile arrangement as U/UC.

The behaviour under irradiation of UO_2 or UC in any of these forms is better, from the point of view of physical stability than unalloyed uranium metal—there is no change in volume. The samples may however develop cracks either due to thermal gradients or due to pressures developed within[16]. It is however felt[25], that it is not necessary to worry about the integrity of the core in a fuel element so long as the cladding remains in-tact.

Moderators[10, 16] *Beryllia* : Apart from graphite, beryllia[16] is the only refractory compound of interest, since the other refractory BeC, tends to be unstable in moist atmospheres. The thermal conductivity of BeO is high and greater than that of most metals at ordinary temperatures; though it decreases rapidly with rise in temperatures; at 1000°C it is still similar to that of mild steel (0.0485 cgs. units). As a result of the high conductivity, beryllia has shown better resistance to thermal stresses than any other oxide under similar conditions.

BeO can be fabricated by any of the available methods, but the common method for moderator purposes is only by hot pressing.

The stability and unreactive nature of beryllia makes it particularly suitable for operation at high temperature in oxidising conditions. However, above 1200°C it is appreciably volatile in the presence of water vapour and as it is toxic is a health hazard.

From the reactor point of view BeO is probably of great interest for smaller type of reactors using enriched fuel, operating at high temperatures with a gas as coolant.

Control rod materials[10, 20, 21, 23] : For this application a number of refractory compounds of high capture cross section elements, boron, hafnium, europium, gadolinium and samarium are suitable. Boron compounds and boron steel have been used in the existing reactors.

Boron forms two stable carbides B_4C and B_6C[20] with melting points over 2000°C. In addition, the borides of the high melting metals of the 4th, 5th and 6th groups are refractory and are stable upto 1500°C, beyond which oxidation becomes appreciable. All the compounds of boron are subject to radiation damage due to the production of helium and the extent of this will prohibit its use in certain circumstances.

B_4C and B_6C[20] are used in powder form in stainless steel tubes for control rod applications; for shielding purposes they can be either hot pressed or incorporated into polyethylene, rubber or aluminium (Boral).

Because of their very high capture cross-section compounds of hafnium, europium, samarium and gadolinium are of interest for use in high temperature reactors. Though studies[21] on these materials are in progress it is not likely that any ceramic material would have sufficient impact strength to be used as control rods. Either the material has to be used in a powder form in metal tubes or suitable cermets of these oxides have to be developed for this application.

Summary

Ceramic materials, especially the oxides and carbides, which hitherto were only used as refractories in the melting of nuclear metals, hold promise for application in high temperature reactors. They have a high melting point, adequate strength at elevated temperatures and are more resistant to corrosion compared to metals. These properties are desirable for their use at higher temperatures, in the reactor core.

The materials for use in the reactors have to be extremely pure and should have a density close to theoretical. These materials are fabricated by suitable modifications of the conventional ceramic techniques. Isostatic or hot pressing techniques are found to be very suitable.

Some oxides and carbides are already being used in the core of reactors, e.g. UO_2 for fuel elements, BeO for moderator, and B_4C for control rods. It is likely that with the development of reactors operating at elevated temperatures, ceramic materials might find more applications. But upto the present interest has been mainly in developing suitable fuel elements.

The ceramic materials have a low thermal conductivity and a low thermal shock resistance, the values for the oxides being much lower than for the carbides. The low thermal conductivity results in an excessive temperature build up in the fuel element core. The difficulty can be overcome, either by reducing the size of the fuel element or using disperse systems of the fissile material.

Little definite information is available on the nature of radiation damage to ceramic materials. Available information on UO_2 shows that

the radiation damage is much less than in the metal. The cracks developed in massive UO_2 in service, are not considered a disadvantage, so long as the cladding is not disrupted. The probability of this occurring is not much, as the UO_2 undergoes no volume change on irradiation.

The existing data on the performance of oxides and carbides in particular and ceramics in general justifies further developmental studies on ceramic materials, to provide materials for high temperature power reactors.

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Appendix—I. Melting points of some refractory oxides and carbides

Material	Chemical Composition	Melting Point °C
Alumina		2015
Beryllia	BeO	2550
Calcia	CaO	2600
Hafnia	HfO_2	2777
Magnesia	MgO	2800
Silica	SiO_2	1728
Thoria	ThO_2	3300
Urania	UO_2	2280
Zirconia		2677
Beryllium carbide	Be_2C	2150
Boron Carbide	B_4C	2450
	B_6C	
Hafnium Carbide	HfC	3887
Thorium Carbide	ThC	2628
	ThC_2	2655
Uranium Carbide	UC	2250
	UC_2	2350—2400
Zirconium Carbide	ZrC	3530

Discussions

Dr. R. C. Despande, (*Institute of Armament Studies, Kirkee*) : Is it possible to use "sweat cooling" for reactor fuel elements made from uranium oxides and carbides?

Mr. L. M. Wyatt, (*U.K.*) : "Sweat Cooling" has been considered but the pressure required to remove sufficient quantities of heat from the fuel elements, with fine passages through them, would be too great. Furthre the coolant would become contaminated with the fission products.

Mr. K. Singh, (*Poona*) : Is it possible to fabricate articles of various shapes by melting the refractory oxides? Temperatures to melt such oxides are now available in plasma jets.

Mr. L. M. Wyatt, (*U.K.*) : Yes. Carbides can be melted and cast in the argon arc furnace. The casting of UO_2 rods was described in the recent Paris Conference. I doubt whether the accuracy of the shapes and the soundness of casting is sufficient for nuclear fuel elements. These processes, however, are obviously capable of development.

SPECIAL PROBLEMS IN THE SINTERING OF BERYLLIUM OXIDE

*By R. Caillat**

The sintering of beryllium oxide has some special features arising from its nuclear applications, certain chemical properties and toxicity.

Sintered beryllium oxide is used as moderator or reflector; the nuclear considerations for these purposes specify high density and low thermal neutron capture cross section of the product.

For example, beryllium oxide used by J. C. Koechlin, J. Martelly and V. P. Duggal[1] for measurements on the diffusion length of thermal neutrons had a mean density of 2.95 (Theoretical density: 3.02) and an impurity-content so low that the total capture-section for the neutrons considered was less than 2 millibarns.

2.6 tons of the sintered product were used in the form of bricks, faces of which had been machined to the precision of 1/10 mm.

There demands, with respect to purity and density, are severe for the process of sintering. As regards purity requirements based on nuclear considerations, it is to be noted that whereas the exclusion of the smallest contents of neutron capturing elements is called forth, presence of graphite even in appreciable quantities will be quite acceptable.

Thus, the bricks referred to above contained less than 0.3 ppm of boron but nearly 1% graphite.

The sintering of beryllium oxide has been found to be more difficult in comparison with that of the more usual oxides such as alumina and zirconia.

According to previous German investigations, reported by Ryschkewitsch[2], density of 2.7 gms/cc was the maximum that could be reached even after firing at 1900°C. A recent Brush Beryllium Co. report[3] on sintering of beryllia at 1700-2000°C metions the realisation of density of only 2.0-2.6 gms/cc.

There are certainly many variables in these investigations which require to be more precisely defined and there is no doubt that many statements would need revision as a result of some of the investigations now in progress. But, for the immediate technical projects, we have also to take into account the situation as it exists.

Further, mention must be made of two properties of beryllia, which

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though not quite peculiar to it alone, assume exceptionally intense role in its case. The addition of a few percent of an extraneous oxide leads to an abrupt fall in its fusion point from 2500°C to the usual sintering furnace temperature of 1600-1800°C[4]. The risk of contamination from the refractory containers thus becomes very serious.

Then, in presence of water vapour, beryllium oxide becomes volatile at 1100°C[5-9] which complicates the sintering operation. This aspect is highly important because of the extreme toxicity of dusts and aerosols of beryllia: it is now accepted practice that an operator should not generally be exposed to atmospheres containing more than 2 μg of BeO per m^3 of air.

Sintering under pressure, introduced a few years back, helps to resolve these difficulties [10-12]. Sintering under pressure is distinguished from natural sintering by the fact that the piece to be sintered is kept under compression in a die, in this case graphite, during the entire run of sintering. This method applied to beryllia leads regularly to very high densities, higher than 2.95. The only impurity introduced into beryllia in this method is graphite and this does not increase the total effective capture cross section of the product. Protection against the hazards of beryllia toxicity is easy to devise in the operations involved and the method consists essentially of the following three states :

Preparation of the oxide
Sintering
Machining to specifications

Preparation of Beryllium Oxide suitable for Sintering under pressure

Three beryllium compounds have been used for the preparation of the oxide intended for sintering :

—basic acetate of beryllium $[(CH_3CO_2)_2\ Be]_3\ BeO$
—sulphate SO_4Be
—hydroxide $Be\ (OH)_2$

The basic acetate is volatile under vacuum above 100°C, permitting its purification by repeated sublimations. When decomposed at 600-700°C, a particularly pure oxide is obtained which (in USSR) is sintered in vacuum under pressure[13]. The basic acetate is also sufficiently soluble in chloroform to allow its purification by extraction.

In France, however, these processes have been used only for preparation of small quantities of beryllia[14] required for analytical or scientific purposes.

The sulphate and hydroxide are the products, that have been studied on a large scale in this country. The purification of these compounds is effected by the usual chemical treatments (dissolution in aqueous solvents followed by precipitation). The work has been done by Com-

pagnie Pechiney, in close association with the French Atomic Energy Commission within the frame-work of atomic collaboration between India and France[15].

The oxide is obtained by calcination of the sulphate or the hydroxide.

Calcination of beryllium sulphate

The table below summarises the main points of the chemical behaviour of Be $SO_4.4\ H_2O$ heated from room temperature to 1000°[16].

Temperature	175°C	300°C	400°C	620°C	775°C	820°C	920°C	1000°C
% water elminated	50%	98%	99%	100%				
% SO_3 eliminated				traces	50%	98%	99%	100%

The operation is convenient: dispersion of the oxide in air or its fluidisation by the gaseous products of decomposition, sometimes encountered and found cumbersome in the calcination of hydroxides, has never been met with for sulphate.

Of course, elimination of the last traces of sulphate takes long time even at 1000°C, but it is neither necessary nor always desirable[11].

The exact physical characteristics of the oxide obtained depend on the conditions of calcination, that is to say, on the highest temperature reached, the time taken in attaining it and on the time for which it is maintained. In general, the oxide obtained at 1000°C is composed of crystallites with dimensions smaller than one tenth of a micron, whilst at 1500°C, considerable recrystallisation occurs within a few hours, leading to dimensions above 1 to 2 microns.

The specific surface of the oxide obtained at 1000°C is of the order of $20 m^2$ per gm, and is lowered within one hour at 1500°C to a little below $2\ m^2$ per gm.

All these results are strictly for the oxide obtained from pure beryllium sulphate. The figures given below will serve to show the contents of impurities picked up in a typical run.

Elements		Content in ppm
Al	...	180
B	...	0.4
Ca	...	160
Cu	...	50
F	...	<1000
Fe	...	100
K	...	80
Li	...	1
Mn	...	≤ 5
Na	...	150
Si	...	950

Calcination of beryllium hydroxide

Beryllium hydroxide is known under three allotropic forms :

(i) An amorphous form, obtained by the neutralisation of a solution of beryllium salt by an alkali. It is a gel, filterable with difficulty having a variable composition.

$$Be(OH)_2 . x\ H_2O$$

(ii) An "Alpha", metastable crystalline form in which the amorphous form is transformed naturally within a short period. This transformation is accelerated when the amorphous gel is agitated near the boiling point in dilute alkaline medium.

(iii) A stable "beta" form, obtained by hydrolysis of solutions of alkaline beryllates. The "beta" form, accompanied by the "alpha" form is also obtained by agitating the amorphous gel in a concentrated and hot alkaline solution.

The "beta" form presents considerable advantages from the point of view of the preparation of pure hydroxide; it gives dense precipitates, easy to filter and wash; and treated under certain conditions, it is suitable for sintering under pressure[17].

These considerations have guided the investigation which led to the invention of a process permitting the direct precipitation of beryllium hydroxide in the "beta" form[18]. The process consists in introducing simultaneously a solution of beryllium salts and an alkaline solution into a suspension of precipitated beryllium hydroxide (which serves as a primer) contained in a vessel provided with agitators, maintaining throughout a pH of 6 to 8.5 and temperature of 100°C. It is convenient to make a paste of the hydroxide, which can be readily done either with a mineral acid or a solution of beryllium salt. This facilitates the process of sintering by reducing the swelling encountered in this step and is found helpful in subsequent sintering under pressure[11].

The thermal decomposition of beryllium hydrate, into either of these three forms, begins at 250°C. In the vicinity of 650°C, more than 97% of water is eliminated. One percent of water is, however, still retained at 1000°C, but this does not introduce any difficulty during sintering[16].

The physical characteristics of oxides obtained under identical thermal conditions vary with different forms of the hydrate used as starting material : amorphous hydrates and the "alpha" with low apparent density (lower than 0.1), give oxides of indefinite structure which sinter with great difficulty. "Beta" hydrates are of the greatest interest, because the oxide obtained by their calcination at 1000°C is suitable for sintering, having specific surface of the order of a few tens of m^2 per

gm. They consist of crystallites with dimensions less than 0.1 micron. Raising the calcination temperature results in decrease of specific surface and increase of grain size, the latter attaining at 1500°C, a value of the order of a micron.

Calcination Practice

The calcination can be conducted in a silica crucible upto 1050°C without impairing the purity[19]. The crucible was 30 cm in diameter and 1 m. in height. The duration of thermal cycle was 15 hours, and the maximum temperature attained 1050°C.

For a typical example, the impurity-contents measured in a representative sample of the standard calcined oxides are given below :

F	B	Si	Fe	Al	Impurity
<100	$\angle 0.3$	70	105	<100	ppm

Total impurity: 2.95%

H_2O and SO_3 expelled on heating

Sintering of Beryllium Oxide under pressure

Laboratory study : The conditions for sintering under pressure of beryllium oxides prepared by different methods, have been determined in the laboratory on compacts of 3 cm-diameter and 1.5 cm height[12].

The sintering apparatus (fig. 1) includes a rigid frame, and a jack to apply the desired pressure on the product to be sintered via a column of alumina refractories. A pressure gange 0-6 tons, situated on the upper end of the support and resting on the refractory column, measures the force applied on the compact in the course of sintering. The graphite mould is heated by high frequency induction. The temperature is measured by a Ribaud type optical pyrometer. The accuracy of measurements, allowing for the different sources of error (regulation of high frequency generator, definition of light source sighted on, etc.), is such that the temperature variations in the neighbourhood of 1600°C are of the order of $\pm$ 10-15°C.

Preparation of samples : The beryllia used is kept free of moisture. Before sintering it under pressure, it is cold compacted in a steel-die at a pressure of 2600 kg/cm^2.

Sintering : The compacts are placed in a graphite die. A pressure of 30 kg/cm^2 is applied initially to the column. The pressure helps to keep the apparatus in position and ensures sufficient air-tightness, so

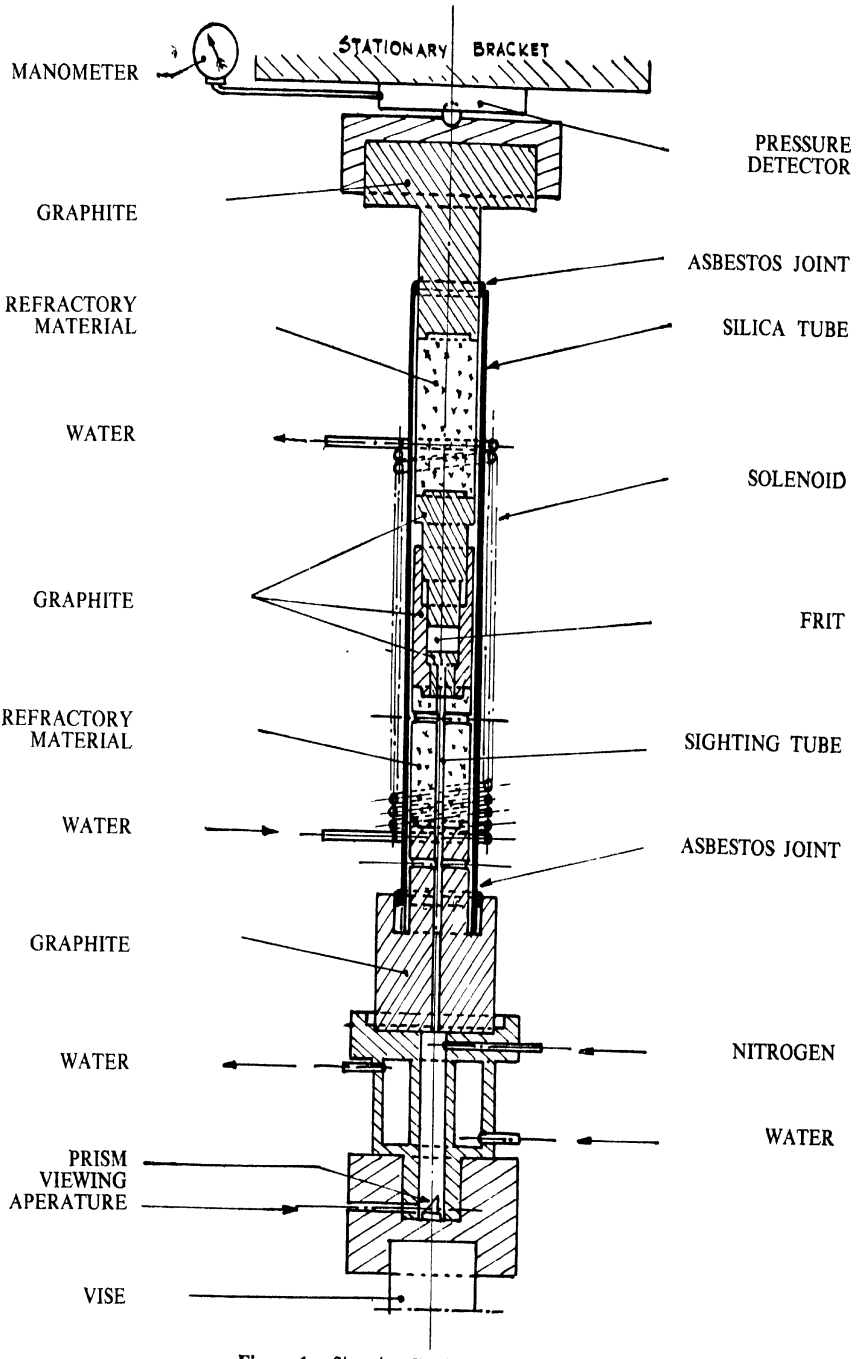

Figure 1.—Sintering Equipment

that the graphite die can be protected from oxidation by the current of nitrogen sweeping through the sighting tube.

The temperature is raised to about 1600°C within 20 minutes. The sintering pressure is applied only when the temperature of testing is reached. The pressure and temperature are maintained constant during the entire sintering experiment.

Results : For the comparison of different products we have selected their density as principal sintering parameter. All other conditions remaining equal, especially the raw material, form and dimension of compacts and compacting of the latter in the cold, the following physical factors may be considered as affecting the process of sintering:

sintering temperature
time during which this temperature is maintained
pressure under which sintering is carried out.

From beryllium oxide obtained by calcination of a "beta" hydroxide under the conditions previously described, density of 2.95 is obtained at 1600°C with a pressure of 200 kg/cm^2 applied for 30 minutes.

Indentical results are obtained, under the same conditions of sintering, from the oxide resulting from calcination of beryllium sulphate at 1000°C.

In the event of appreciable recrystallisation taking place when heated for one hour at 1500°C, density of the sintered product, other conditions remaining the same, is always lower. It is independent of the method used for obtaining the oxide.

Conditions of sintering

200 kg/cm^2 applied for 30 minutes at 1550°C

—BeO, from $BeSO_4$ calcined at 1500°C for 1 hour ;
specific surface : 1.6 m^2/g
density obtained : 2.79 gm/c.c.

—BeO, from $BeSO_4$ calcined at 1000°C for 2 hours;
specific surface: 18 m^2/g
density obtained: 2.88 gm/c.c.

Practice of sintering under pressure

The materials and operations are similar to those we have just described for laboratory scale work. The graphite mould is designed to yield a sintered products of 100 x 50 mm dimensions. Heating is done by induction, using a 60 KVA generator.

The starting material is the oxide obtained by calcination of

$Be(OH)_2$. The powder is charged into the die. The sintering temperature is reached within 1½ hours. To complete the operations in less than 4 hours for this size of the sintered product, temperatures higher than 1600°C are required. The usual sintering temperatures deviate very little from 1850°C.

Machining of Sintered Beryllium Oxide Bricks

Sintered bricks are machined on a horizontal grinding machine using a diamond wheel. During machining, the piece is cooled with kerosene oil at the point of cutting. The machine is enclosed in an enclosure maintained under high suction through powerful ventilation. These precautions protect the operator from beryllia dusts.

The faces of bricks are thus finished to a precision of 1|100 of millimeter.

After this machining, the bricks are washed and wrapped up. Subsequent handling is done with all the precautions necessary for a product of great purity. The impurity-contents as controlled in a brick of standard quality are given below :

Fe	Si	Al	Ag	Cu	Mg	Mn	Pb	Ni	
$\angle$ 50	$\angle$50	100	<0.5	<10	<5	<3	<3	<3	ppm

The nuclear quality of different lots of bricks is checked by oscillation tests in a channel of the pile E. L. 2.

Conclusions

In conclusion, the sintering under pressure of beryllium oxide obtained by calcination of "beta" hydrate has permitted the preparation of several tons of precisely machined bricks of pure and dense beryllia.

However, numerous investigations remain to be done in this field :

to state precisely the behaviour of beryllium oxide submitted to radiation in the course of its use in piles.

to improve the methods of fabrication and sintering in order to diminish the cost price of sintered oxide.

These are the fields where scientific investigations can lead directly to tremendous technical advancements and it is this realisation which led the Indian Atomic Energy Commission on one hand and the French AEC on the other, to draw and pursue actively a common programme of work on beryllium oxide.

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Discussions

Dr. M. R. Srinivasan : I wonder if Dr. Caillat would tell us about the irradiation damage in beryllium oxide.

Author's Reply : The literature mentions a considerable effect of the radiations on the properties of beryllium oxide, such as, for instance, variations in length of several percent for integrated fluxes of the order of 10^{20}. The comparison of the various results obtained in different laboratories is rendered difficult because of the lack of precise knowledge of the nature of the neutrons whose integrated flux is mentioned. However, and subject to verifications in progress, we have never observed such effects. In any case, an English work published in the Acta Crystallographica, agrees with us, in observing only a very weak variation of the parameter of BeO, along the axis C, for similar integrated fluxes. To our knowledge, it is the thermal conductivity of beryllium oxide which is most affected by radiation. We hope to be able to specify this variation shortly.

POWDER METALLURGY IN NUCLEAR ENGINEERING

*By Henry H. Hausner**

Powder metallurgy methods for the fabrication of nuclear reactors components are already widely used. Fuel elements, control rods, moderators, and materials of construction are presently manufactured by powder metallurgy. It is, however, believed that the application of powder metallurgy as a fabrication technique for reactor components will be more extensive in the future with the steadily growing nuclear engineering industry.

Powder metallurgy as a technique for forming metal parts has many advantages which are of importance in nuclear engineering. Reference is especially made to :

(a) The minimum loss of material during processing, which is important, especially with respect to the high cost of the raw material;

(b) The possibility to obtain grain structures which are desirable and favorable for the behavior of the material in the radiation field;

(c) The forming of metals at temperatures far below the melting point, and, in this way, avoiding work at temperatures where unfavorable crystal structures develop;

(d) The formation of alloys at low temperatures;

(e) The combination of metals and non metals which are already widely used for the fabrication of dispersion-type fuel elements.

For some of these materials conventional powder metallurgy methods of compaction and sintering, or hot pressing, are already applied. It has been found, however, that special metallurgical techniques, such as powder rolling and slip casting, can be extremely useful for the production of special nuclear reactor components.

One has to keep in mind, however, that handling of certain powders used in reactor technology is not so easy as the handling of copper, iron, or any other ordinary metal powder. For example, zirconium in the form of very fine powder particles is highly pyrophoric ; fine beryllium powder particles are highly toxic; the powders of uranium and thorium are both toxic and pyrophoric; and plutionium powder is toxic, pyrophoric, and dangerous to be handled on account of its radiation. This is not only true for these metals in powder form, but also for compounds of any of these, such as the oxides, carbides or

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nitrides. Handling of these powders, therefore, has to be done with greatest care. Dry boxes for manipulating these powders have been well developed by the skill of mechanical engineers, and actually permit safe handling of any of the above mentioned dangerous materials.

"Powder Metallurgy in Nuclear Engineering" will be the subject of a forthcoming book, to be published in December, 1957, by the American Society for Metals, and edited by this author.

The special role of powder metallurgy in nuclear engineering

Metals prepared by powder metallurgy differ in many ways from metals made by conventional methods.

A. *Crystal Lattices in Powder Metallurgy Products* : Fabrication of metal powders can be achieved by several mechanical, chemical, or electrochemical methods. According to the method of fabrication, the powder particles differ in shape, size and structure.

Any powder particle is characterized by the high ratio of its surface area to its mass or volume. This is an important feature with respect to the particle structure, inasmuch as the surface crystal lattices are usually different from the body lattices; they show a large amount of point defects, such as lattice vacancies, dislocations or other disturbances, so that one may consider these surface lattices as highly disordered[1,2]. It has been proven that the radiation effect in a material is closely connected with the degree of disorder in the structure, and that a material with higher degree of disorder in the crystal lattices is more resistant to radiation effect than when characterized by ordered lattices.

The lattice distortions in the metal powders progress further during compacting under pressures which vary between 5 and 50 tsi, but which are still much greater in the contact areas where the metal powder particles touch each other. During the next step in powder metallurgy, i.e., sintering, the lattices rearrange to a certain extent but very seldom end up in ordered structures, although, by some heat treatment after sintering conditions, the lattice structures may change to ordered ones. The disordered lattices resulting from the powder metallurgical processing may make a material more resistant to radiation damage, and this is definitely one advantage powder metallurgy has to offer as a method for fabricating materials for nuclear power reactors.

B. *Grain Structures in Powder Metalludgy Products*[3] : Grain growth in powder metallurgy products during sintering is different from the normal grain growth in conventionally fabricated metals treated under similar heating conditions. This matter is of greatest importance inasmuch as the grain size of a material frequently determines its behavior under irradiation.

The equations governing grain growth in metals are well known. One distinguishes between continuous grain growth and grain growth by cold work and recrystallization. The higher the degree of cold work, the more nuclei are formed for recrystallization and, therefore, the smaller are the grains in the structure under development. Grain growth can be hindered by the addition of impurities to the metal. This inhibits grain growth or at least decreases considerably the rate of grain growth. The compact pressed from metal powders contains a large amount of highly cold-worked powder particles. Between the powder particles there are voids or holes, which take approximately 10 to 30% of the compact volume. On account of the high degree of cold work in the powder particles, even before, but especially after, compacting, a large number of nuclei for recrystallization are formed, which leads, in a general way, to small grain sizes. Besides this fact, one has to consider further that the voids between powder particles act in a manner similar to impurities, that is they hinder or delay the grain growth during sintering. This reduction of grain growth during sintering is especially effective during the earlier stages of sintering. As sintering progresses, the voids become smaller and most of them finally disappear. Both facts—the high degree of cold work in powder particles and the presence of voids—have the effect that powder metallurgy products are usually characterized by smaller grains in the structure, although the grain sizes can be increased by a heat treatment above sintering conditions, following the actual sintering operation.

C. *Alloys by Powder Metallurgy*: It is well known among nuclear engineers that certain alloys made from fissionable materials with small alloying additions are more favorable with respect to radiation effect and corrosion than the pure fissionable material, although the mechanisms causing these effects are not yet fully understood. Alloys can be prepared by conventional melting processes in liquid state reactions, or they can be made by powder metallurgy in solid state reactions. The end product may differ in grain size; however, this may not have any extensive effect on the corrosion resistance of the alloy.

The preparation of certain alloys by powder metallurgy offers some advantages, especially in alloys made from very heavy metals such as uranium, and very light metals. Ordinary melting of two components with quite a difference in density frequently results in segregation of the two components, and one or even more remelting steps may have to be added in order to obtain a homogeneous alloy structure. Remelting, however like any other long-term, high-temperature process, involves the danger that the metals may pick up definitely undesirable amounts of gaseous impurities. Mixing the two alloying components in the form of powder particles to a high degree of uniformity offers no difficulties, and any subsequent compacting or sintering operation does not disturb the homogeneity of the mixture. Although the large total surface area of the powder particles would usually permit the pickup of gases, powder metallurgy sintering usually occurs at tem-

peratures far below the melting temperature of the metallic components, and this low temperature process lowers the possibilities of picking up gaseous impurities. All this indicates that alloys prepared by powder metallurgy may be very useful and offer advantages compared with conventionally prepared alloys in the fabrication of components for nuclear reactors, where impurities play such an important role.

D. *Metallic Compounds and Cermets*: It is a well-known fact that certain combinations of metals, which do not form alloys, can be made by powder metallurgy methods. These metal combinations are known as compound metals, such as tungsten-copper or molybdenum-silver combinations as used for electrical contacts. In these compound metals, one metallic component is present, either in the form of discrete particles within the matrix of a second component, or in the form of a metallic framework interwoven with another metallic framework.

The materials known as cermets—combinations of metallic and nonmetallic components—are similar to the compound metals and cannot be made by any other method than by powder metallurgy. The development of these cermets is usually directed towards products for high-temperature purposes, such as parts for gas turbines or jet propulsion engines, and the ceramic components are usually carbides, borides or other metal compounds bonded together by metals such as nickel, copper, etc. These cermets offer certain advantages when developed for nuclear engineering purposes. The APPR fuel elements containing a core of stainless steel with UO_2 particles uniformly dispersed in the steel matrix are fabricated in this way. Control rods can also be manufactured by this method.

The solid fuel element developed as a cermet could play an important part in any reactor design, and powder metallurgy fabrication methods are required for these types of materials.

E. *Bonding for Heat Transfer Purposes*: Certain reactor parts, such as fuel cores, must be clad by another metal in order to prevent corrosion and to prevent the escape of fission products into the coolant, under reactor operating conditions. The "cladding" sometimes has to be well bonded in order to create best conditions for heat transfer which plays an important role in many reactor components.

A perfect metallurgical or diffusion bond between the metal part to be protected and the protecting metallic cladding, which prevents corrosin, is very desirable in many cases, and powder metallurgy offers some advantages in this respect. Diffusion of one metal into another metal usually requires high temperature or long-term treatment at lower temperatures; both these conditions are not always in the range of possibility for production operations. In order to lower the diffusion temperature or decrease the diffusion time, the metals should have

high surface activity, which usually results in an increased diffusion rate.[4] Metal powder particles, on account of their high curvature and their large number of lattice defects, usually diffuse at lower temperatures, and within a shorter time, than cast metallic bodies.

Fig. 1 shows, in a schematic way, the rate of diffusion between :

(1) cast metal (a) and cast metal (b)
(2) cast metal (a) and sintered metal (b)
(3) sintered metal (a) and compacted but unsintered metal (b)
(4) metal (a) and metal (b), both compacted and unsintered.

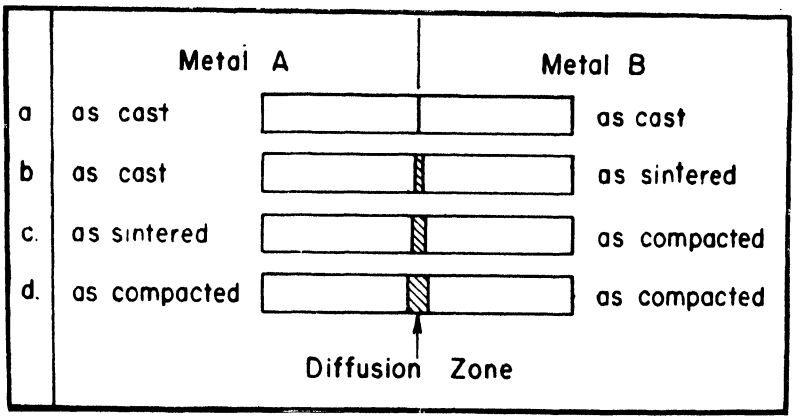

Figure 1.—Diffusion between two metals, A and B, under constant temperature, time and pressure conditions as a function of their method of preparation

From this schematic representation, one can recognize that minimum diffusion occurs between cast metals and that the fastest diffusion rate occurs between metal powders in the unsintered state. Experience has shown that sintered metals diffuse easier than cast metals. This fact makes powder metallurgy interesting with respect to the cladding problems in the development of reactor components, inasmuch as conditions can be created which result in perfect heat transfer while miniminzing other deleterious effects.

The Powder Metallurgy of Fuel Materials

Solid fuel elements are to be made either of metals, ceramics, or metal-ceramic combinations.

Metallic fuel elements may consist either of pure uranium or thorium, or alloys of either of these metals with each other, or with other metals. The alloys usually offer the advantage of better corrosion resistance and are also less affected in the irradition field.

Ceramic elements may consist of the oxides, carbides, or other compounds of uranium or thorium. Plutonium compounds are also under consideration. Ceramic fuel elements have the advantage usually of better behavior under irradiation and greater corrosion resistance. They have the disadvantages that they have a relatively low heat conductivity, and do not withstand temperature shocks.

Cermet fuel elements are of the so-called dispersion type, which contain uranium compounds, such as UO_2 in form of powder particles dispersed in a matrix of aluminium, stainless steel, zirconium, or other metals.

Solid fuel elements are used in a great variety of shapes and sizes, such as plates, rods, slugs, tubes or other shapes. For practically any shape a fuel core material can be made by powder metallurgy, even in cases where subsequent rolling, extrusion, or swaging is necessary to bring the element into its final shape.

The following chapters will briefly discuss the fabrication of fuel core materials for metallic, ceramic, and cermet-type elements.

A. *Uranium*[5] : Uranium metal is much too ductile to be mechanically comminuted. Uranium powder, however, can be made by hydriding solid uranium at approximately 225°C. and decomposing the hydride in vacuum at approximately 300°C. While hydrogen is being passed over the metallic uranium, uranium hydride falls off the solid uranium in form of an extremely fine powder.[6] Both powders, the metallic uranium as well as the uranium hydride powder, do not compact to high densities. Uranium powders, however, compact to a fairly high strength and can be handled without any difficulty whereas uranium hydride powder compacts can hardly be handled because of their low strength, even when compacted at fairly high pressures.

Fig. 2 shows the effect of compacting pressure on the density of uranium powder compacts; even when compacted at 75 tsi, the green density is less than 75 percent of theoretical density. Fig. 2 shows, further, that sintering uranium powder compacts at temperatures close to the melting temperature of the material (m.p.=1133°C) does not result in a completely dense material.

Extensive experimental work has been done on the powder metallurgy of uranium during the last few years by the author, and the results of this work are condensed in Fig. 3. This schematic representation shows that re-pressing of sintered uranium hardly helps to increase the density of the sintered material, even when pressures as high as 175 tsi are applied for re-pressing. There is only one way to obtain a perfectly dense, pore-free uranium by powder metallurgy, and that is by hot pressing. Compating uranium powders in vacuum at approximately 10 tsi at a temperature of 600°C for just a few minutes results in a material of 100 percent density. Like many

other hot pressed metal powders, the finished material is of a fairly low ductility. However, the ductility can be consistently increased by subsequent heat treatment.

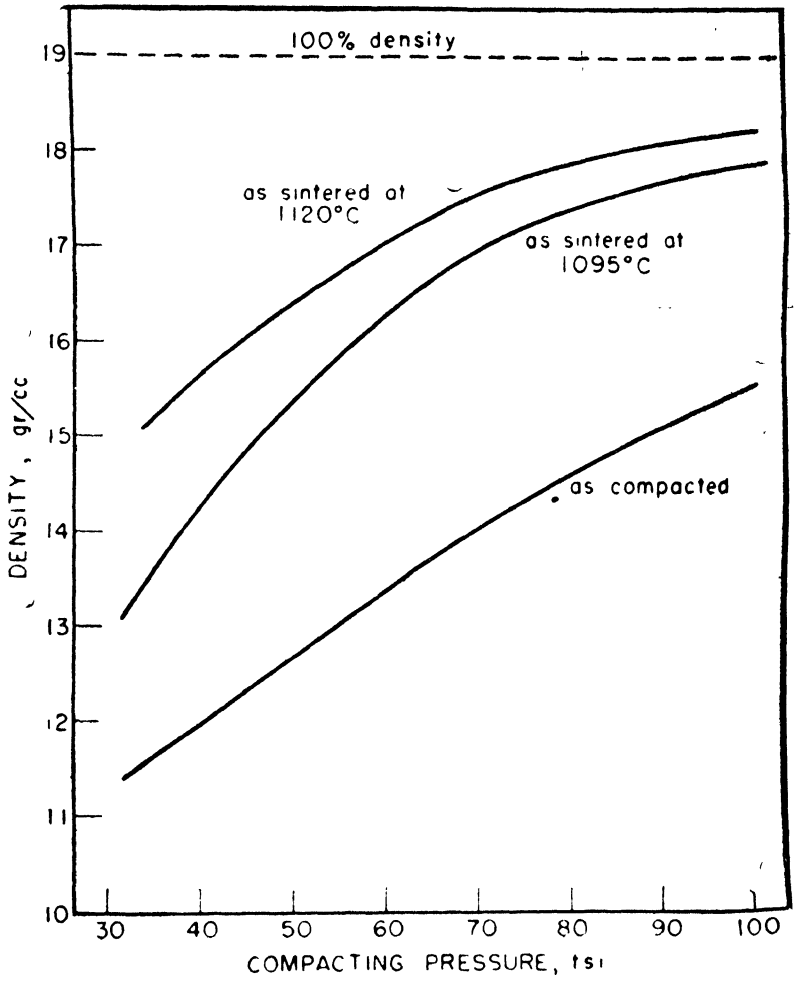

Figure 2.—Effect of compacting pressure on the density of a "green" and sintered uranium powder compact

This hot-compacted dense uranium is interesting in many respects. Uranium undergoes several phase changes: The orthorhombic alpha-phase changes at 663°C to the tetragonal beta-phase, which changes at 764°C to the body-centered-cubic gamma phase. Any uranium made by melting and casting has to be heated to the α-β-γ phase and goes through the same phases during cooling. During this process large grains form in the beta and gamma temperature range and are then

characteristic of the structure of cast uranium. It is known that large uranium grains behave very badly under irradiation.

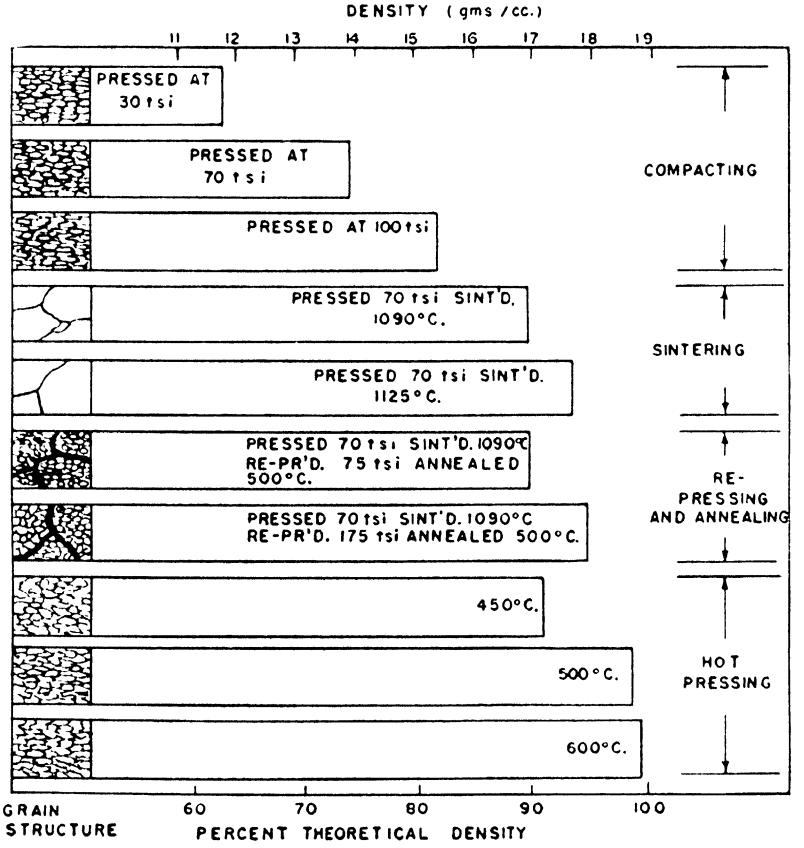

Figure 3.—Density and grain structure of uranium produced by various powder metallurgical treatments

Metallic uranium powder is made by decomposition of the non-metallic uranium hydride at approximately 300°C, which uranium metal powder is then hot pressed at 600°C. This hot pressed solid uranium has never been exposed during processing to any other temperature range than that of the alpha phase, has never had an opportunity to obtain any large grains in the beta or gamma range, and therefore is characterized by a highly desirable uniform fine-grained structure, as indicated in Fig. 3. The effect of temperature on the densification during hot compacting of uranium powders is shown in Fig. 4.

A fine grained uranium structure can also be obtained by cold compacting, sintering, re-pressing and annealing. The grains formed in this way are practically as small as those obtained during hot compact-

ing. There is, however, a great difference between these two fine grained structures. The fine grains in the hot pressed uranium are perfectly randomly oriented, whereas the fine grains in the re-pressed and annealed material are sub-grains within the coarse grains from

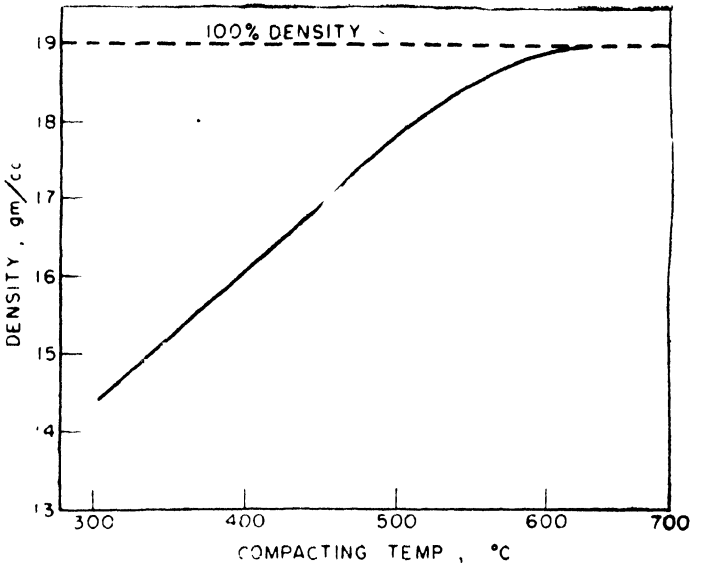

Figure 4.—Density of hot compacted uranium powder vs. compacting temperature (20 tsi)

which they were formed and are therefore oriented in practically the same way as the former coarse grains. The material with the sub-grained structure is strongly affected by irradiation, whereas the material with true, randomly oriented, fine grains behaves well in the radiation field.

Table I—Effect of the method of preparation of thorium on the powder particle size.

Method of powder preparation	Particle size, μ
Decomposition of hydride ThH_2	10-50
Electrolytic	20-140
Calcium reduction of oxide ..	20-100
Sodium reduction of oxide	20-100

B. *Thorium* : Thorium is used in nuclear reactors as a most valuable breeder material for the supply of the fissionable U_{233}. The powder metallurgy of thorium has been extensively studied in the United States[7] as well as in other countries. At the Atoms-for-Peace Conference in Geneva, in 1955, Professor G. A. Meerson, from the Moscow Institute for Non-Ferrous Metals, presented a paper on "The Powder Metallurgy of Thorium,"[8] thus indicating Russia's general interest in the powder metallurgy of reactor materials.

Table II—Mechanical properties of sintered and repressed thorium specimens

Type of Powder	Sintering temperature, °C	Characteristics of speciments	Density g/cc	Tensile strength kg/mm²	Yield strength kg/mm²	Elongation %	Hardness kg/mm²
Electrolytic	1100	Sintered	11.30	14.7	7.8	28.0	50
	1300	„	11.35	15.2	8.0	30.0	53
	1300	Repressed without annealing	11.60	14.6	13.8	0.0	84
	1100	Repressed and annealed	11.59	16.6	8.0	35.0	53
	1300	Repressed and	11.62	16.6	8.3	43.0	51.3
Calcium Reduced	1100	Sintered	10.77	17.6	11.0	10.3	69.0
	1100	Repressed and annealed	11.51	21.7	13.5	20.0	70.0
	1300	Repressed and annealed	11.55	21.1	13.7	17.4	70.0

Thorium powder can be prepared by several methods, as shown in Table I[9]. The decomposed thorium hydride powder permits production of the most perfect sintered thorium compacts of 100% density. Thorium hydride forms by passing hydrogen over solid thorium at approximately 750°C; this is a solid material which can be easily ground to a powder of any desired particle size and converted into a high purity thorium powder by decomposition in vacuo. However, this process is not necessarily the most economical one; processes using thorium powder made by the electrolysis of fused salts or by calcium or sodium-reduction of the oxide will probably be more economical. The calcium reduction of thorium oxide occurs by adding calcium chloride to the oxide in powder form and heating the mixture up to 1000° or 1100°C. in vacuum or an inert gas. The reduction in an inert gas is to be preferred because the rate of calcium evaporation can be lowered in this way. Meerson reported that a maximum yield in production can be obtained by adding 40% calcium chloride by weight to the charge, and described this process in some detail.

The compactability of thorium powder depends on the method of powder production. Thorium powder made by the decomposition of the hydride can be compacted practically to its theoretical density. Table II[8] shows the mechanical properties of sintered and re-pressed thorium specimens made from electrolytic and calcium-reduced thorium powders, respectively. This table shows that the densities of the compacts made from electrolytic thorium powder are higher than those made from calcium-reduced powder, and yet these lower-density compacts have a greater strength than those with the higher density. With respect to elongation, the electrolytic thorium powder compacts are far superior to the calcium-reduced compacts. The effect of sintering temperature on the mechanical properties of electrolytic thorium powder compacts is shown in Fig. 5. The hardness of these sintered compacts is practically independent of the sintering temperature between 900° and 1500°C. This is not the fact for calcium-reduced or decomposed-hydride thorium compacts, in which the hardness depends strongly on the temperature of sintering.

C. *Uranium Dioxide* : While solid metallic fuels offer the advantages of good neutron economy, good thermal conductivity and high resistance to thermal shock, their phase changes and low strength at elevated temperatures hardly permit their use in high specific-power reactors. Ceramic fuel materials, on the other hand, offer the advantages of adequate strength at elevated temperatures, low thermal expansion, good corrosion resistance and stability against radiation damage.

A comparison between the melting temperatures of various compounds of uranium and other, more common, refractory materials shows that UO_2 has the highest melting point (2800°C) of the possible ceramic fuel materials. Examination of the physical properties of UO_2

shows that this compound is chemically and thermally stable and, therefore well suited for use as a high-temperature nuclear fuel.

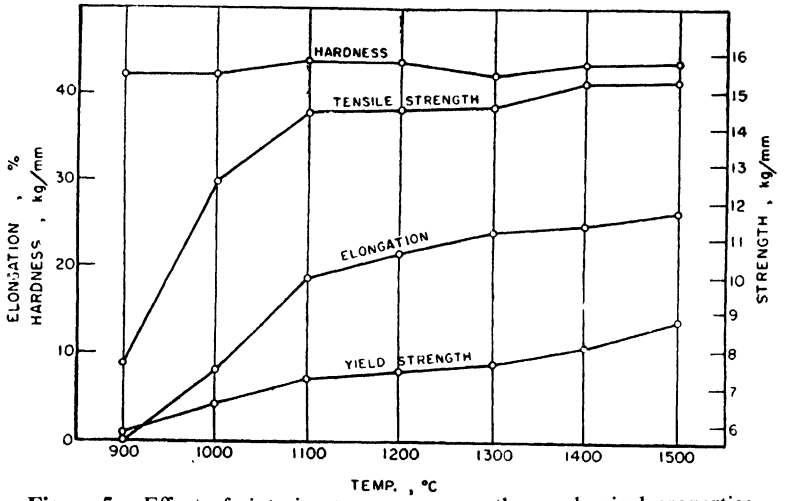

Figure 5.—Effect of sintering temperature on the mechanical properties of electrolytic thorium powder compacts, sintered at various temperatures. (According to G. A. Meerson)

Uranium dioxide powder can be produced by several different methods, most of which use an aqueous uranyl nitrate solution as a raw material. With the addition of H_2O_2 to the solution, uranium peroxide is precipated. The precipitate is converted to uranium trioxide by heating. If ammonia is added to the uranyl nitrate solution instead of H_2O_2, ammonium diuranate is precipitated, and this also can be thermally decomposed to uranium trioxide. The reduction of UO_3 to UO_2 can easily be accomplished in a hydrogen atmosphere.

The production of uranium dioxide enriched in the isotope U^{235} includes a gaseous-diffusion step with the uranium in the form of the hexafluoride, UF_6. This can then be converted to ammonium diuranate, and subsequently to any oxide desired.

The UF_6 process has been worked out at Mallinckrodt Chemical Works in St. Louis. Cylinders of UF_6 are heated by an electric blanket, with the fluoride compound vaporizing through pig-tail pipes into a water tank. In water, UF_6 rapidly hydrolyzes into HF and uranyl fluoride (UO_2F_2). The uranium then precipitates as ammonium diuranate when aqueous ammonia (25-30%) is added in the hydrolysis tank. After the compound is filtered, washed and dried, it is decomposed to U_3O_8 with steam. When the U_3O_8 has been dried, it is reduced with hydrogen at high temperatures to UO_2.

The bulk density and particle size of the resultant UO_2 depend on the density and particle size of the parent material. The temperature

of reduction of the parent material likewise influences both the crystalaite size and particle size of the UO_2.

Uranium dioxide must be ball-milled to fine particles to be capable of being sintered to the desired high-density material. During ball milling in air, the uranium dioxide usually increases in oxide content. The increase in oxygen content depends largely on the ball-milling conditions and especially on the duration of the milling process. Prolonged ball milling results in the comminution to particles with an increased specific surface area and, therefore, greater oxygen pickup.

Table III—Increase in oxygen content of UO_2

UO_2 prepared from	UO_2 mean diameter μ	Time of exposure to air at room temperature	Analysis value of x in $UO_2 + x$
U_3O_8	0.38	1 month	0.022
,,	1.3	2 days	0.012
,,	1.36	3 days	0.005
,,	0.56	3 days	0.012
UO_3	0.45	2 days	0.006
UO_3	0.059	1 day	0.135

Very frequently a solid lubricant, such as stearic acid or polyethylene glycol, is blended into the powder before it enters the hopper. The blend is then fed from the hopper into the cavity of the die, in the lower end of which is a smooth-fitting punch. The amount of powder placed in the die is regulated by the position of the lower punch in the die cavity. After the hopper is withdrawn, the upper punch enters the die and compresses the powder. Compressing the powder in steel dies at pressures of 10,000-100,000 psi results in compacts with densities that depend on the particle size of the powder (see Fig. 6). Large parts can also be hydrostatically pressed in rubber molds at 30,000-45,000 psi[11].

The rate of densification for uranium dioxide powder compacts depends on the sintering temperature, the powder particle size and the excess oxide content of the compound. The sintering operation generally takes place at temperatures well below the melting point of the compound—usually between 1600° and 2100°C. Small additions of TiO_2 permit sintering at about 200°C lower, if desirable.

Uranium dioxide picks up oxygen when exposed to air. In powder form it acquires this excess oxide content even when stored in glass containers. Since it is impracticable to keep UO_2 in an oxygen-free environment, particularly during compacting, some increase in oxide content is unavoidable. Table III shows that the amount of increase is dependent in part on the particle size and on the time of exposure[12]. The fact that UO_2 picks up oxygen when exposed to air is frequently

overlooked but is of extreme importance in its effect on the sintering process.

The effect of particle size on the bulk density after sintering at 2000°C for 30 min can be seen by referring back to Fig. 6. The fine powder particles, which compact to a low density, sinter to considerably higher

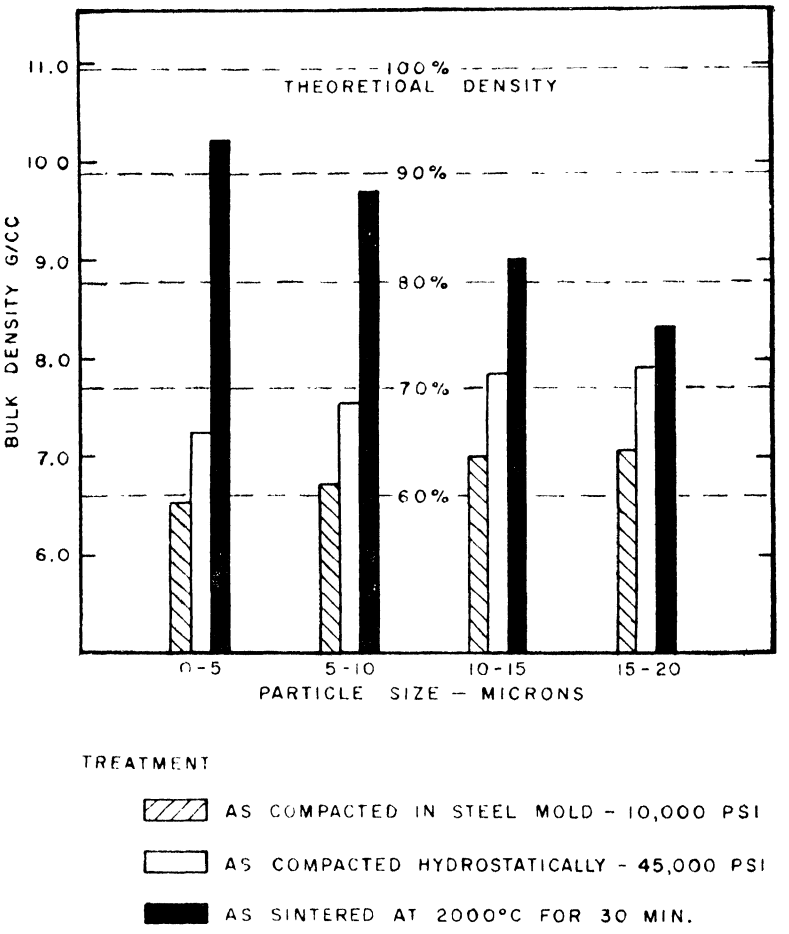

Figure 6.—Density of green compact (unsintered) ranges between 6 and 8.6 g/cc, depending on powder particle size—finer powders compact to lower densities than coarser ones.

densities than the coarse powders that compact so well. Densities of 10 g/cc or higher can be achieved by close correlation of sintering temperatures and sintering time.

The sintering of uranium dioxide compacts should occur in a hydro-

gen or inert atmosphere. Sintering in air is not recommended because it would result in the reaction

$$UO_2 \rightarrow U_3O_8 \rightarrow UO_2$$

with a corresponding change in density from

$$11 \rightarrow 8.4 \rightarrow 11 \text{ g/cc.}$$

This kind of density change would result in a complete fracture of the compact during sintering.

D. Alloys : Power metallurgy methods are not applied solely to the fabrication of parts from individual metals, but also to parts made from alloys. A small amount of an alloying constituent to uranium makes this metal less susceptible to radiation damage but more resistant to corrosion.

There are two possibilities of fabricating alloy parts: (a) compacting and sintering alloy powders, and (b) intimate mixture of the alloying components in powder form, compacting the mixture and formation of the alloy in solid state reaction during sintering.

The technique of compacting and sintering alloy powders is identical with the technique to form pure metals by powder metallurgy. The method to form the alloy from the components in powdered form during sintering is different in so far as the time of heat treatment during sintering is not determined by the rate of densification alone, but also by the rate of homogenization of the alloy. As a general rule, we may say that the time for complete homogenization during sintering is usually longer than the time for just obtaining highest possible density.

The technique for forming alloys by solid state reaction during sintering is attractive for many nuclear engineering purposes.[13] Some of the alloys to be used in nuclear reactors contain uranium, one of the heaviest metals existing. The preparation of alloys consisting of this heavy metal and a second metal of considerably less density by ordinary melting and casting procedures, (for example the preparation of uranium-aluminium alloys), has its difficulties. In the molten state, segregation frequently occurs between the two components of such different weight, and double, or even triple, melting must be applied in order to obtain a homogeneous alloy. Powder metallurgy offers the advantage that even metals with entirely different specific densities can be uniformly mixed in powdered form, and the mixture can be compacted and sintered. The formation of the alloy is then a function of the sintering temperature and time, and no segregation between the components will occur.

The powder metallurgical method for making alloys also permits close control of the grain size. Fig. 7 shows the formation of the useful

zirconium-uranium alloy; it shows the interdiffusion between the two component particles in solid state reaction, the rate of which depends on the sintering temperature.[14]

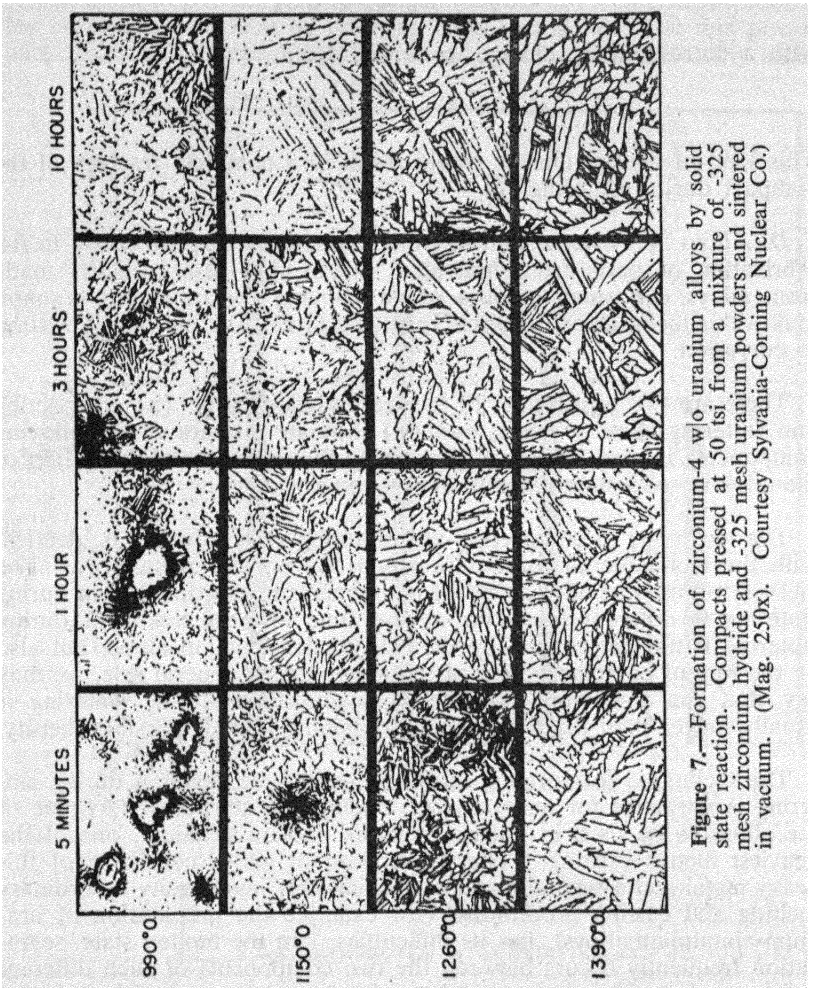

Figure 7.—Formation of zirconium-4 w/o uranium alloys by solid state reaction. Compacts pressed at 50 tsi from a mixture of -325 mesh zirconium hydride and -325 mesh uranium powders and sintered in vacuum. (Mag. 250x). Courtesy Sylvania-Corning Nuclear Co.)

Uranium alloys are of extreme interest for the reactor designer. Uranium-thorium alloys or uranium-beryllium alloys can also be made by the above method.

E. Cermets : Combinations of metals and non-metals, known as cermets, are of importance for many applications, especially however as high temperature materials. They are also of extreme interest to reactor designers[15] and should be discussed here briefly inasmuch as they cannot be made by any other method than by powder metallurgy.

Cermets presently in use or under consideration are of the following composition: UO_2 in powder form dispersed in a matrix of aluminum, stainless steel, or zirconium, or uranium carbide particles in stainless steel. Fuel elements made from this type of cermet material will withstand high temperatures, irradiating and corroding conditions. Because of their metallic components cermets are more resistant to temperature shocks than ceramic materials, and their heat conductivity is also improved by the metallic filler between the ceramic particles. Their thermal expansion is fairly low, depending on the relative amount of the metallic and the ceramic components. In order to prevent fission products from penetrating into the reactor coolant, the above listed cermet cores must be clad, usually by the same metal of which the matrix consists.

UO_2-containing cores must be made by powder metallurgy. The main requirements are utmost distribution of the active UO_2 particles in the metal matrix, precise overall dimensions, and perfect bond between the cermet core and the cladding material. Greatest care has to be taken in mixing the UO_2 particles, which are usually of larger size (—100+325 mesh) than the finer (-200 mesh) metal powder particles. The amount of UO_2 in the mixture may vary between 10 and 60% according to the type of fuel element and the degree of enrichment.

Fuel elements of the dispersion type are presently fabricated in plate and tubular shapes. The principal methods for fabricating a cermet or dispersion-type fuel plate can be briefly described as follows :

(a) Blending of the components for the fuel core in powder form
(b) Compacting of the mixture of powders
(c) Sintering the compacts
(d) Coining the sintered compact to precise dimensions
(e) Insertion of the coined compact into a metal frame (so-called picture-frame)
(f) Covering the picture frame with top and bottom cladding sheets
(g) Welding of the assembly
(h) Hot and cold rolling to final thickness
(i) Trimming to final dimensions.

The powder metallurgy procedure of steps (a) to (e) is fairly simple. The pressures to be applied depend on the type of metal powder (not below 50 tsi for stainless steel), and the amount of UO_2 particles. Uranium dioxide does not react during this process with the matrix metals aluminum, stainless steel, nor zirconium, and the bond between the UO_2 particles and the metal matrix is therefore a purely mechanical one. Processing steps (e) and (f) are shown in an "exploded" view of the composite fuel plate prior to rolling, in Fig. 8.

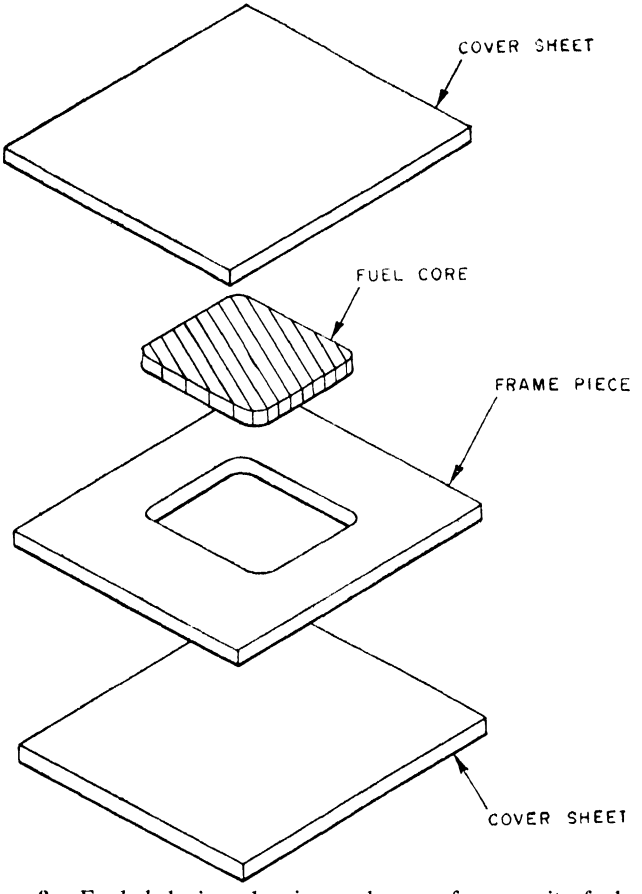

Figure 8.—Exploded view showing make up of composite fuel plate prior to rolling

During rolling the fuel core elongates considerably, and changes in length in the ratio of 1 to 12 are customary. During the elongation of the cermet material the structure becomes oriented, as shown in Fig. 9. This orientation of the UO_2 particles in cermet cores is not harmful at all as long as the formation of continuous UO_2 chains (stringers) is prevented.

The process for making tubular fuel elements also uses powder metallurgy methods, but entirely different from the method for fabricating plates. Storchheim[16] mentioned that tubes of this type can be made by drawing, rolling, extrusion, rolling of sheet and then cold-roll forming, and the powder metallurgy approach is described in one of his previous papers[17]. The powder rolling process, which offers many advantages, also for cermet mixtures, will be described below. Fig. 10 shows a cross section of an aluminum tubular fuel element with 65 w/o

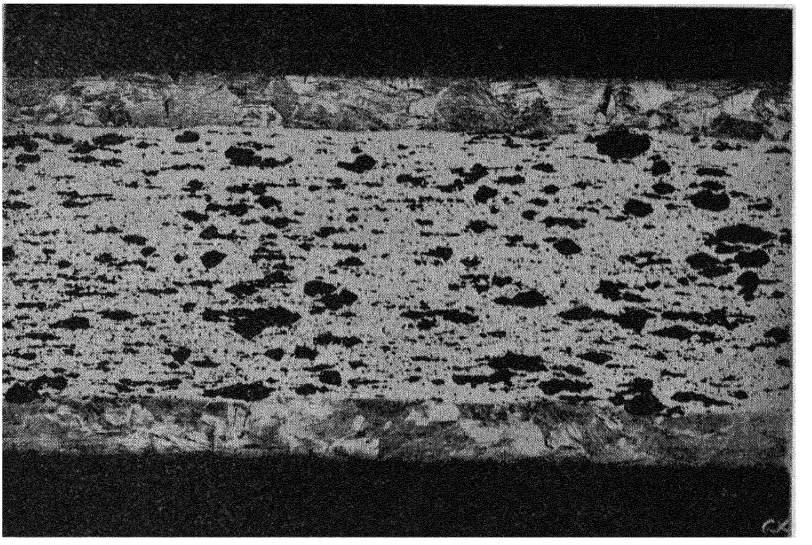

Figure 9.—Cross section of a fuel plate fabricated by the "picture frame" technique. Core : UO_2 in stainless steel. Cladding : stainless steel. (Mag. 100x). (Courtesy : Nuclear Development Corporation)

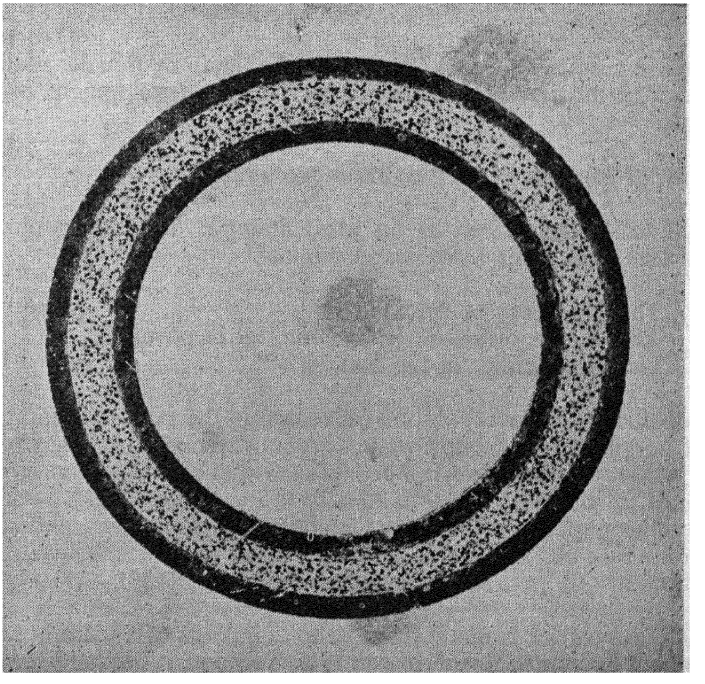

Figure 10.—Tubular fuel element. Core : 65 w|o UO_2 in aluminium Cladding : aluminium (Mag. 15x). (Courtesy : Martin Company)

UO_2 in a matrix of aluminum, aluminum-clad. Fig. 11 shows part of the cross section of a tubular element containing approximately 20 w/o UO_2 in a stainless steel matrix, stainless steel-clad.

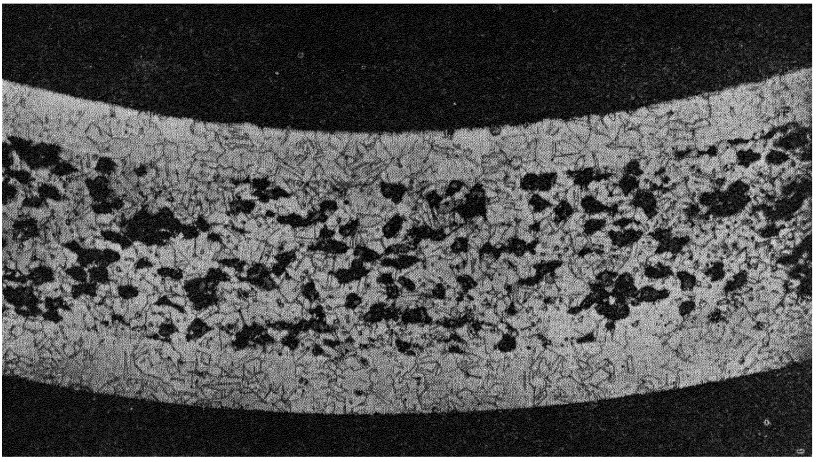

Figure 11.—Tubular fuel element. Core: Approx. 20 w|o UO_2 in stainless steel. Cladding: stainless steel. (Mag. 100x)
(Courtesy: Martin Company)

All these cermet-type fuel cores are to be made by powder metallurgy, and offer an interesting and new aspect in the development of cermet materials.

The powder Metallurgy of Beryllium Moderators

Beryllium is considered as an ideal material for moderators. It is not yet used on a large scale on account of

(a) The high cost of production
(b) The danger of handling the material in powder form
(c) The nonductility of the material.

These obstacles, however, will be overcome in the not too distant future. Several beryllium production plants are under construction, which will permit a considerable lowering in fabrication cost. We have learned—sometimes in the hard way—to handle the toxic beryllium powder and to overcome perfectly the dangers involved in processing, and we have indications that the low ductility of this metal can be improved. Beryllium parts are to be made by powder metallurgy.[18-20]

Beryllium powder is made from lathe chippings of vacuum-cast beryllium billets by comminution in a rolling mill and subsequent pulverization in an attrition mill. Since this metal is very active, it picks up

oxygen during mechanical comminution, and most of the beryllium powders presently used contain 1 to 2 percent of oxygen in the form of oxide, the finer particles containing relatively more than the coarser ones.

Beryllium powder compacts fairly well, as much as can be expected with a brittle material; the effect of pressure on the "green" density is

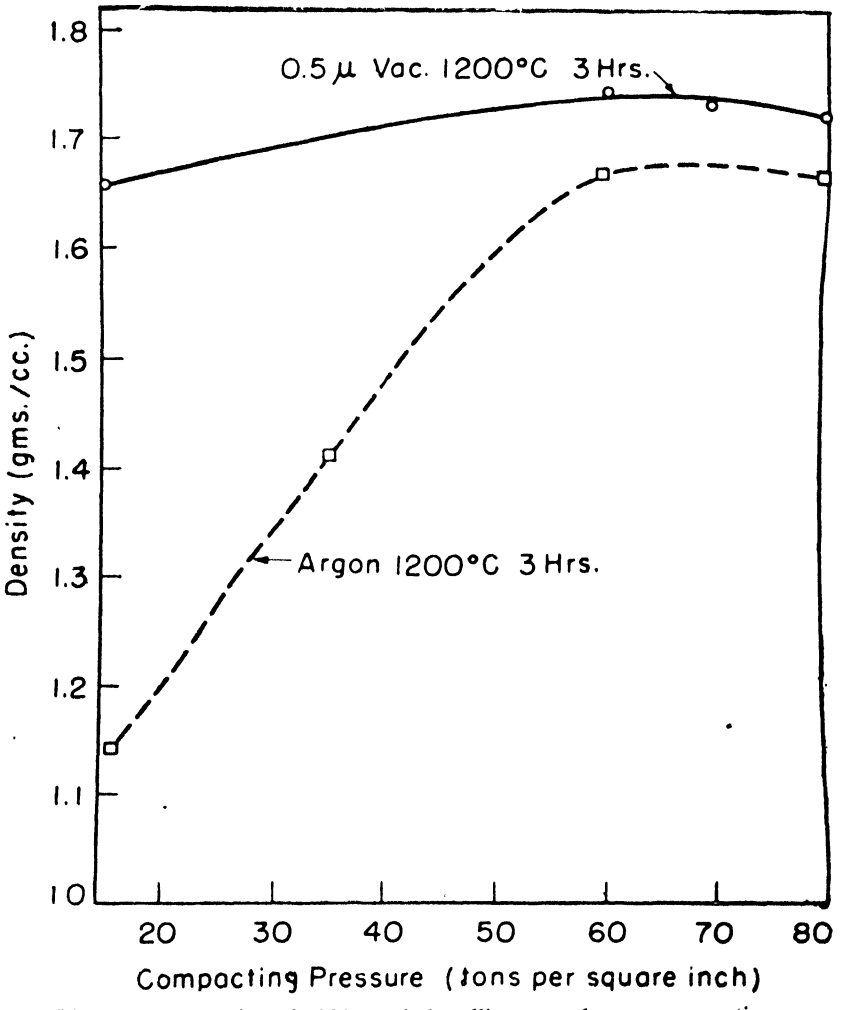

Figure 12.—Density of -200 mesh beryllium powder vs. compacting pressure, as compacted, as sintered in argon and in vacuo

shown in Fig. 12. Subsequent sintering offers many interesting aspects for the metallurgist.

The atmospheric conditions under which sintering of beryllium occurs are of great importance and affect the sintering process very strongly. Fig. 12 shows also the density of beryllium powder compacts sintered in argon and vacuum, respectively, as a function of the compacting pressure. Vacuum sintering results in considerably higher densities than does argon sintering, especially at low compacting pressures. The reason for this phenomenon is as follows: Whereas sintering, i.e., bonding between metal powder particles and densification of the compact, is usually determined by mechanisms such as surface and volume diffusion, another mechanism takes place during sintering of beryllium: namely evaporation and condensation. The mechanism, however, will be effective only by sintering the beryllium compact in vacuum. The less the compacting pressure, the greater the porosity of the compact, the greater the exposed surface of the beryllium powder particles, and in consequence more material will evaporate from the surfaces and condense again around the contact points between the particles. This evaporation and condensation process, however, is hardly effective when sintering occurs under atmospheric pressure in a protective gas such as argon.

Condensation of the beryllium vapor around the contact points increases the bond areas between the beryllium powder particles without contributing to the densification, but, inasmuch as the vapor deposition increases the contact areas, the electrical resistivity of the compact decreases as shown in Fig. 13. The sudden drop of electrical resistivity at a temperature between 600° and 700°C can only be explained by evaporation and condensation as a sintering mechanism. This sintering mechanism in addition to diffusion, however, affects nucleation and recrystallization conditions and therefore the microstructure of the sintered material. The grain growth of beryllium during sintering in argon is shown in Fig. 14. Vacuum sintered material is characterized by a smaller and more uniform grain size. Besides this—and this is the most interesting part in the powder metallurgy of beryllium—the argon-sintered material is hopelessly brittle, whereas the vacuum-sintered material shows some indications of ductility; it can be cold rolled approximately 10 percent, then annealed and cold rolled again. During cold rolling, the characteristic twins form, the number of twins increasing with increasing reduction by cold rolling. The microstructure of the cold rolled material and the disappearance of the twins after annealing is shown in Fig. 15.

In order to obtain a pore-free, completely dense material, the beryllium powder has to be hot pressed. Actually most of the beryllium presently in use is made by hot pressing. There are two methods for compacting at elevated temperature: Hot pressing (1000°-1100°C) at low pressures, or warm pressing (600°C) at higher pressures. Compacting beryllium powders for one minute at 600°C at 25 tsi results in a 100 percent dense material. This material, however, does not possess any ductility.

The Powder Metallurgy of Zirconium

Zirconium in a nuclear reactor is used as a
(a) Material of construction
(b) Dispersion material for uranium-compounds in fuel cores
(c) Cladding material for fuel elements.

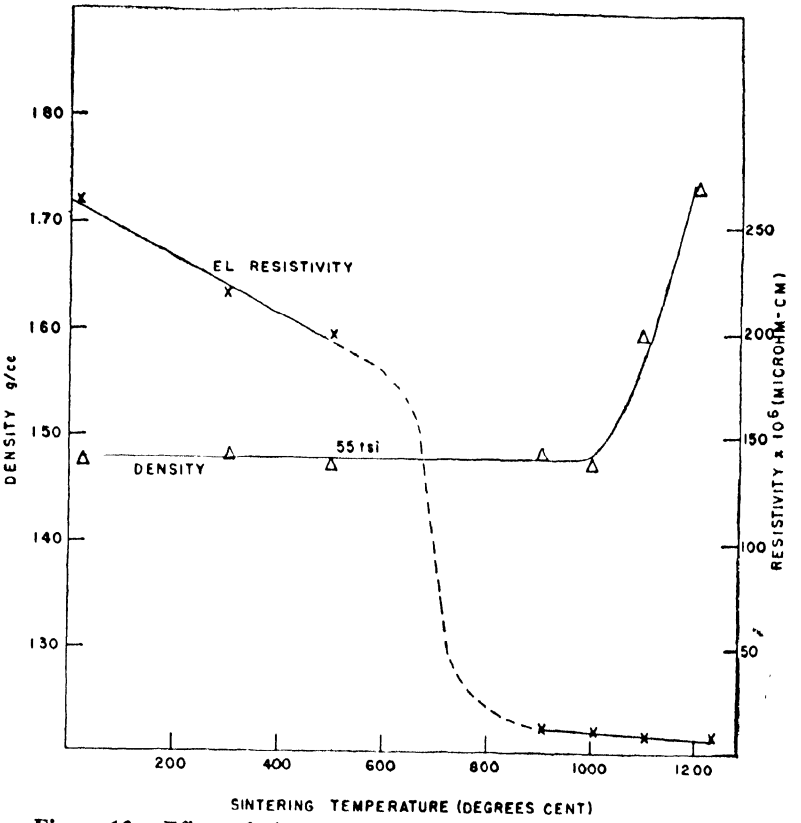

Figure 13.—Effect of sintering temperature on density and electrical resistivity of beryllium. Specimens sintered 3 hrs. in vacuo; measurements at room temperature

There are several processes developed for the manufacture of zirconium in powder form, as shown in Table IV. Regardless of the method of powder preparation most zirconium powders can be compacted without difficulty and sinter to the full density. Actually zirconium is one of the metals best suited for powder metallurgy application. It is an extremely interesting material inasmuch as it permits "activated" sintering, i.e., sintering at an increased rate due to some additional reactions taking place during the sintering treatment.[14]

The following discussion will be concentrated on the application of

powders made by the hydride process; it will cover the powder metallurgy of zirconium hydride, as well as zirconium, powder, obtained by the decomposition of the hydride.

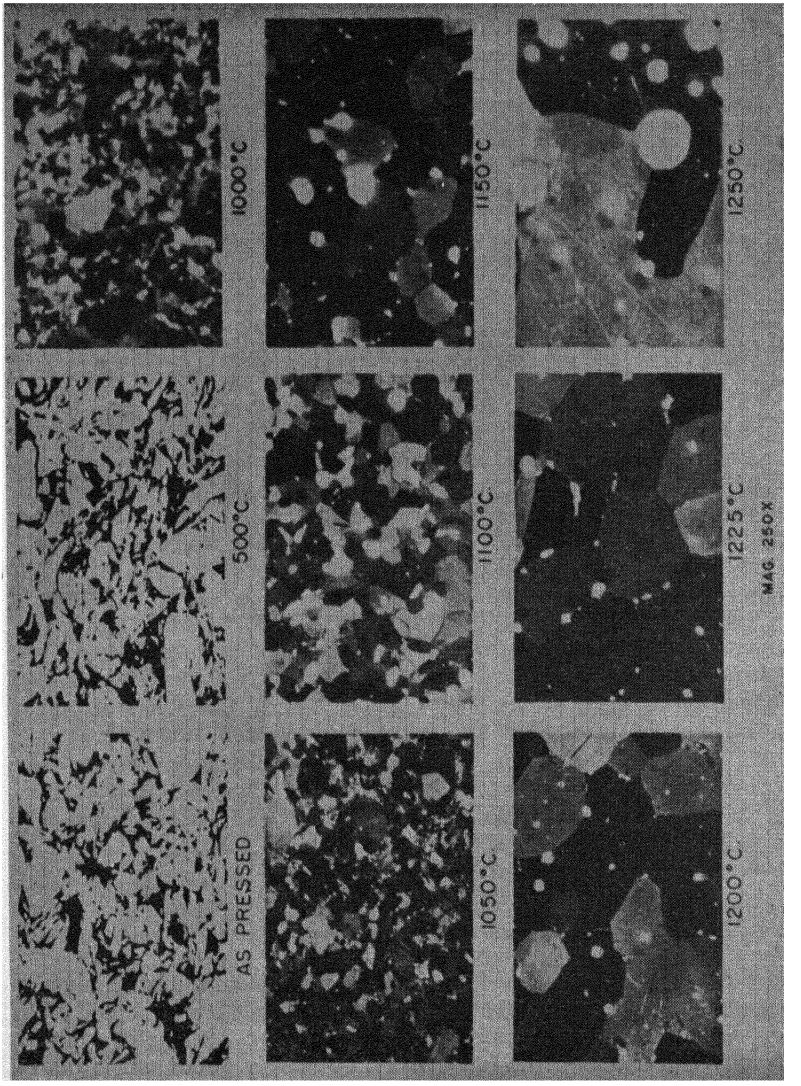

Figure 14.—Grain growth during sintering of beryllium powder compacts in argon for 1/2 hr. at various temperatures (Courtesy: Sylvania-Corning Nuclear Co.)

Zirconium hydride is made by passing hydrogen over zirconium irrespective of whether the solid zirconium is made by the Kroll process (sponge zirconium) or by the DeBoer process (crystal bar zirconium). The temperature most suitable for hydriding these materials is appro-

ximately 800°C. At this temperature the lower hydride, ZrH, forms. During cooling from this temperature in hydrogen, another hydride, ZrH_2, forms at approximately 400°C. Zirconium hydride is a solid material of great brittleness which can be mechanically comminuted to

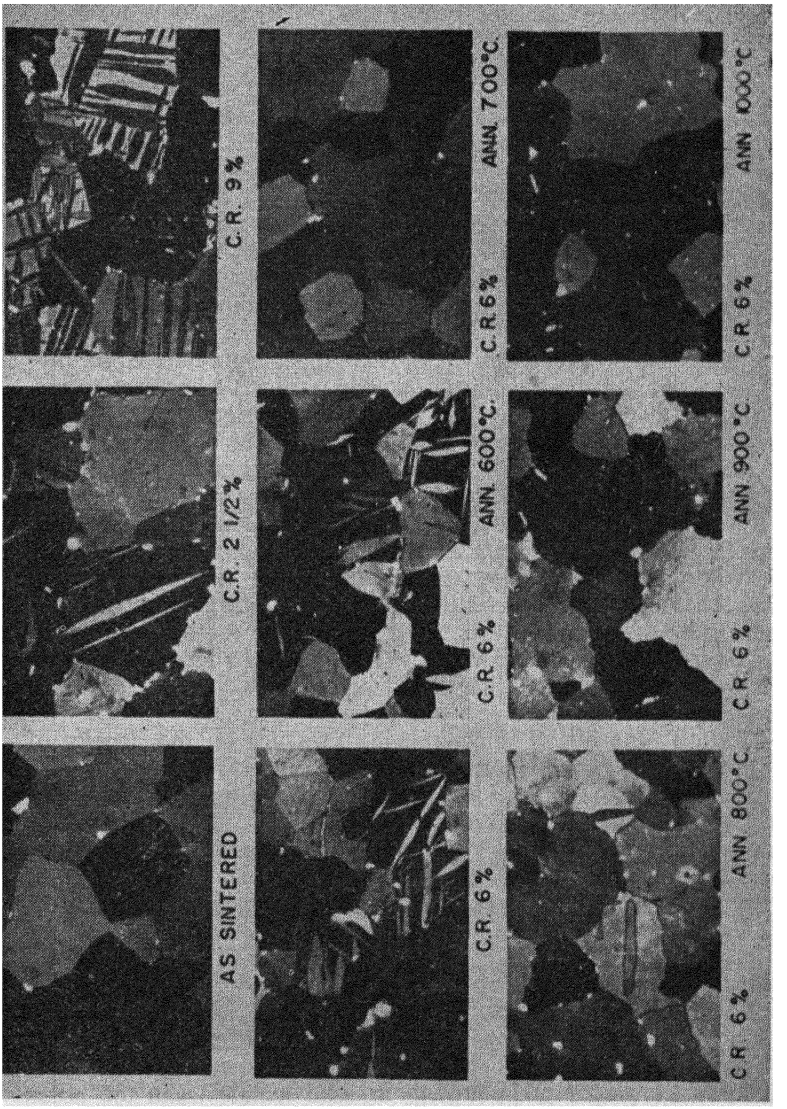

Figure 15.—Cold-working of beryllium. Compacts sintered 3 hrs. at 1|2 hr. (Mag. 250x) (Courtesy : Sylvania- Corning Nuclear Co) 1220°C in vacuc ; annealed

any desired particle size without any difficulty. The zirconium hydride powder can be converted into zirconium metal powder by decomposition in vacuum of 0.05 microns or better, at a temperature of approxi-

TABLE IV

Metal	Method of powder preparation	Particle size in microns
Zirconium	Decomposition of hydride ZrH_2	20-30
	Leaching	15-20
	Calcium reduction of oxide	3-6
	Electrolytic	—

mately 800°C. Both powders, ZrH_2 as well as Zr, compact to fairly high densities at conventional compacting pressures, as shown in Fig. 16. The modulus of rupture of the "green" compact pressed at 50 tsi is 1700 psi for compacts made from zirconium hydride powder and approximately 3500 psi for zirconium metal powder compacts.

During sintering of zirconium hydride compacts in vacuum, the hydride decomposes and the zirconium hydride particles transform to zirconium and the hydrogen evolves. The decomposition of the hydride occurs at approximately the same temperature at which bonding starts between the zirconium particles. For practical purposes, we may say that both processes, decomposition and bonding, take place at approximately the same temperature. During decomposition the zirconium atoms are in an accelerated state and vibrate at amplitudes which correspond, without decomposition, to amplitudes of thermal vibration which are characteristic for considerably higher temperatures. This accelerated state of atomic vibration is probably the reason why sintering, i.e., bonding and densification of the decomposed zirconium hydride compacts, occurs already at fairly low temperatures.

Fig. 17 shows the effect of compacting pressure on the density of pressed and subsequently sintered zirconium and zirconium hydride powder compacts both sintered in high vacuum. This graph indicates that for powders compacted at 60 tsi full density can be reached by simultaneous decomposition of zirconium hydride and sintering for 3 hours at 1260°C, whereas metallic zirconium powder compacts do not densify completely even when sintered for the same period of time at 1320°C.

Densification and grain growth occur simultaneously during sintering, as shown in the microstructures, Fig. 18. The rate of grain growth is slow as long as the density is low, and the voids or pores in the compact hinder boundary movement. The grain growth, however, will follow the well known laws for grain growth in solid metals when the pores in the compact disappear. The time for full densification during sintering depends on the sintering temperature and on the compacting pressure, as shown in Fig. 19. Sintered zirconium is highly ductile and can be cold worked and rolled without any difficulty. Nevertheless, powder-

metallurgically prepared pure zirconium is seldom applied in reactor engineering. The powder metallurgical preparation of zirconium alloys, however, is of great importance for nuclear reactor purposes.

New methods in powder metallurgy for nuclear engineering purposes.

Powder metallurgy products are generally characterized by their fairly simple shape and by small dimensions. Reasons for this are the

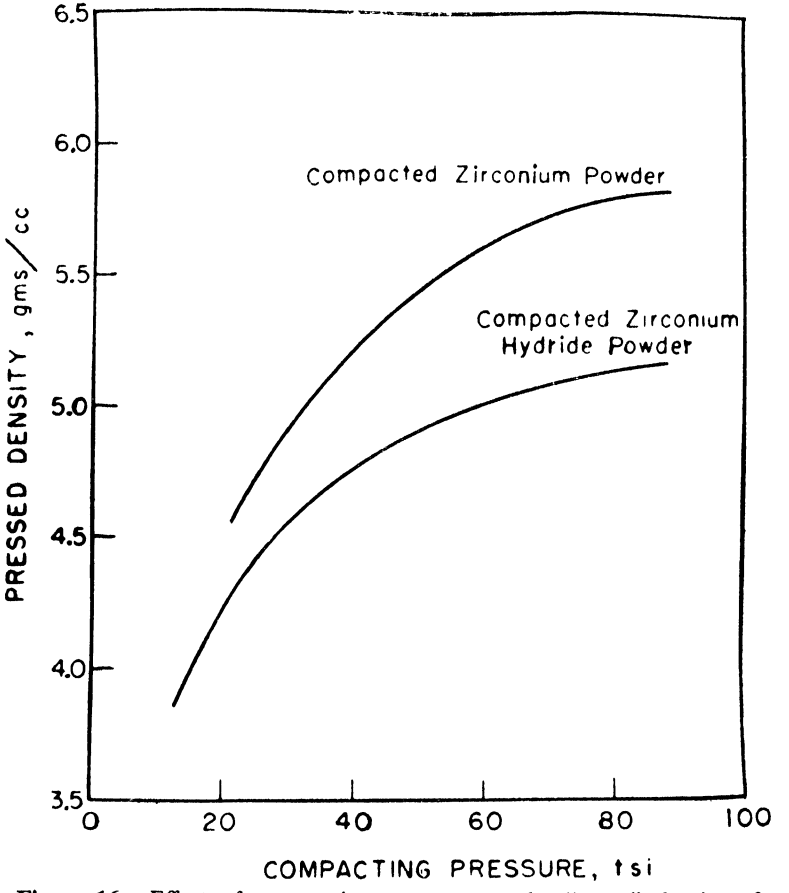

Figure 16.—Effect of compacting pressure on the "green" density of compacted zirconium and zirconium-hydride powder, respectively

limitations in the die design and the capacity of the compacting press. For example in order to press a simple stainless steel plate of 3″ x 15″ side length from stainless steel powder, a hydraulic or mechanical press of 2500 tons capacity would be necessary. New powder metallurgy methods, developed during the last few years, seem to have applications

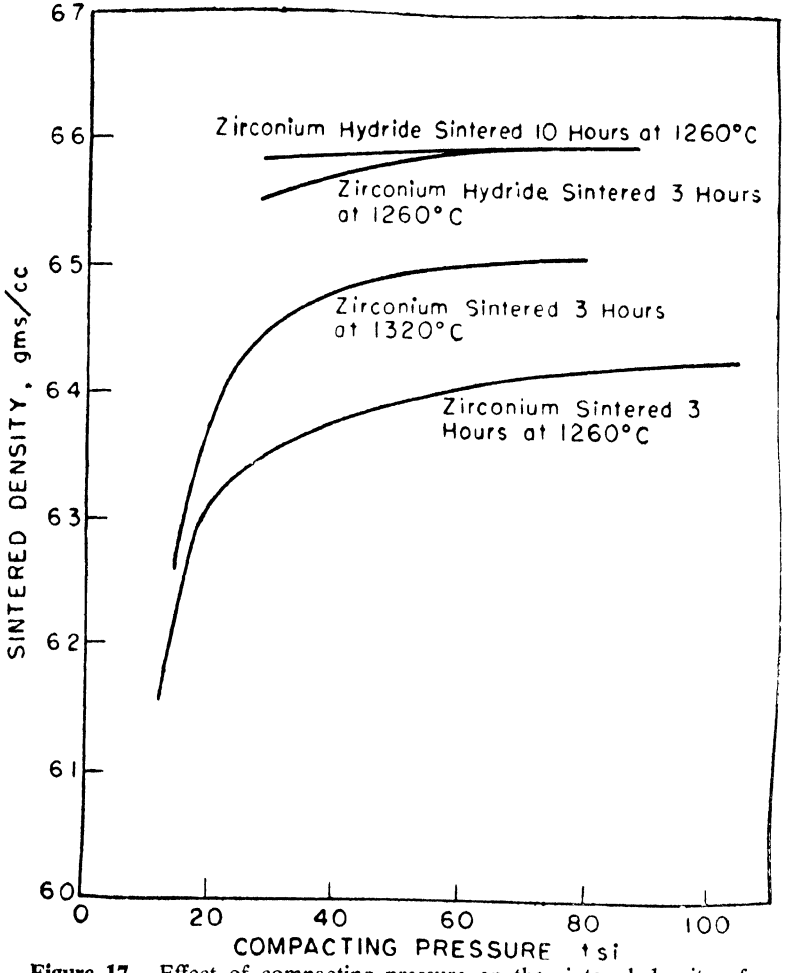

Figure 17.—Effect of compacting pressure on the sintered density of compacted and sintered zirconium-hydride powders (sintered in high vacuum)

in nuclear engineering that would overcome the above outlined limitations of the more conventional powder metallurgy methods of compacting powders in steel dies. I refer especially to the method of powder rolling into strips and sheets, and to the newly developed method of metal powder slip casting. Both methods are of interest for the manufacture of fuel element materials of metallic and cermet nature.

A. *Powder Rolling* : Several years ago, Dr. Naeser, a German metallurgist, developed the process of powder rolling[21], i.e., densification of metal powders by passing them through a horizontally arranged rolling mill, sintering the sheet or ribbon obtained in this way, and rolling

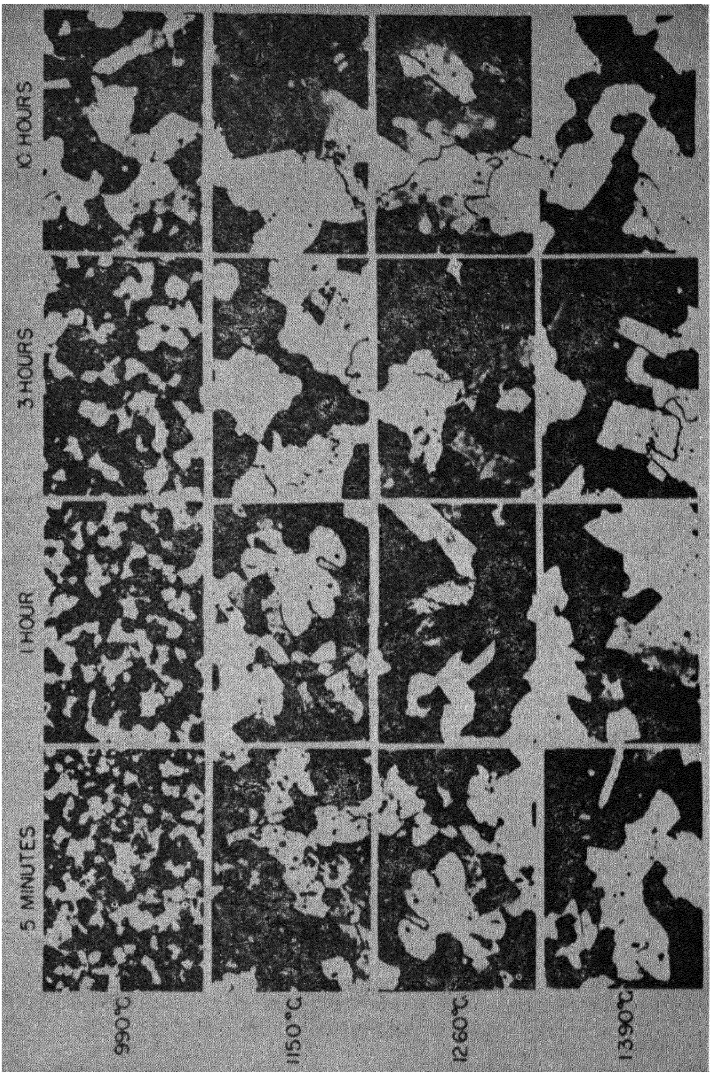

Figure 18.—Effect of sintering temperature and time on the grain structure of zirconium compacts pressed at 50 tsi from -325 mesh zirconium hydride powder and sintered in vacuum. (Max. 250x) (Courtesy: Sylvania-Corning Nuclear Co.)

it again, etc., as shown in the diagram, Fig. 20. The process offers many advantages, such as

(1) forming of a product of almost endless length which could not previously have been manufactured by powder metallurgy;
(2) fairly little orientation in the grain structure, due to the fact that the rolling operation results in densification more than in elongation;
(3) small grain structure.

During the last few years the powder rolling process has been studied and further developed in the United States, and applied to copper, iron, stainless steel, aluminium, molybdenum, zirconium, and other metals, and also to mixtures of metal and ceramic components in powdered form, such as used in dispersion-type fuel elements. Special rolling mills[22] for processing nuclear fuel elements have been developed and the results obtained with powder rolling are considered extremely promising. Very little orientation or stringering of oxide particles in a metal matrix occurs if the powder rolling technique is applied.[23]

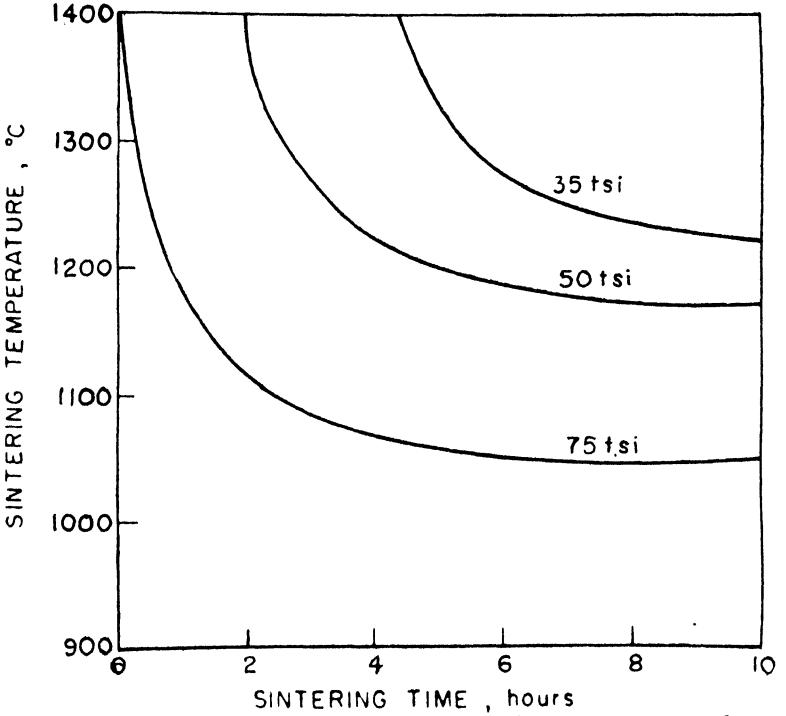

Figure 19.—Isodense lines representing 6.59 g/cc (complete densification) for three compacting pressures. Data for -325 mesh ZrH_2 powder, vacuum sintered

The process also offers advantages for bonding together two layers of metals in powder form; on account of the high activity of the powder particles, the bond between the two layers is extremely strong.

Powder rolling permits fabrication of very thin sheets or ribbons of uniform thickness. The "green" strength is sufficient for handling before sintering.

B. *Slip Casting of Metal Powders* : Slip casting has long been established in the field of ceramics as a method of molding ceramic ware of

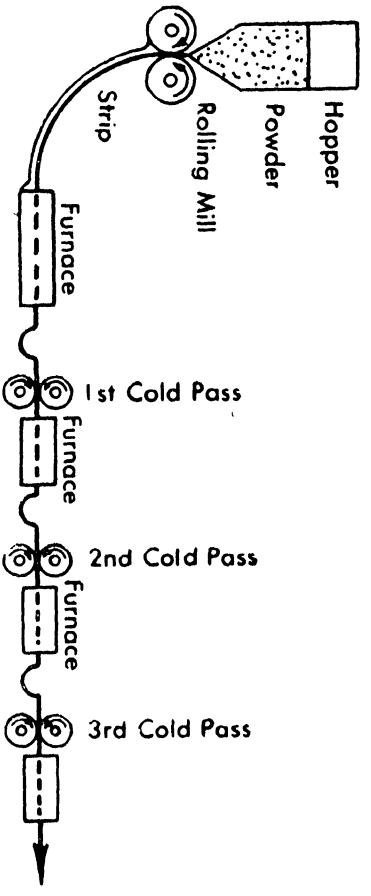

Figure 20.—Flow diagram for production of strip from metal powder

large dimensions or complicated shapes. Now this method is being adapted to the production of metal powder shapes. It merits serious consideration as a new powder metallurgy process and the development work is in progress in several organizations.

To slip cast metal powders,[21] the same procedure used for making ceramic ware is followed. A fluid suspension of metal powder in liquid is poured into a plaster-of-paris mold. The porous mold permits the liquid to penetrate and be absorbed while the powdered metal in the slip dries within the mold. The mold is then opened and the partially dried casting is removed and allowed to dry completely. Then it is fired in a sintering furnace until it reaches the desired physical properties.

The variables of the process are in general similar to those in conventional powder metallurgy, with the exception that no pressing

variables are to be considered. Main emphasis lies in a careful mixture of metal powder particles of various sizes, and in new variables that are of importance, such as the type and amount of deflocculents, added to the slip, and, further, the viscosity and pH factor of the slip.

Considering the above, the following variables are of prime importance in slip casting metal powders: (a) desity of powder particles; (b) process of powder production ; (c) powder particle shape, porosity and diameter; (d) powder particle surface conditions; (e) reaction of the powder with the liquid; (f) density, viscosity and temperature of the liquid; (g) ratio of solid to liquid; (h) amount of air entrapped in the slip; (i) type of deflocculent; (j) pH factor of the slip; (k) rate of drying in the die, which depends on material of the mold and porosity of the mold material; (l) rate of drying after removal from the die; (m) sintering conditions including rate of heating, temperature, time and atmosphere.

This list is by no means complete. The variables listed, numerous as they are, however, are controllable and will definitely permit a fairly high degree of precision in slip casting.

Slip-cast stainless steel powders sintered at 1300°C for 2 hrs result in a sintered product of 7.4 g|cc density, as recent tests have indicated.[25]

The slip casting process is especially of interest for the production of uranium compound-metal mixtures for cermet type fuel cores in the shape of larger size plates.

Summary

Powder metallurgy proves to be a most useful metallurgical technique for the fabrication of nuclear reactor components, especially for fuel elements. The variables which control the powder metallurgy of uranium, thorium, beryllium and zirconium and the oxides of some of these materials, are well under control. Powder metallurgy is the only technique which permits fabrication of the so-called matrix-type fuel elements, the core of which consists of a cermet material, usually with UO_2 particles dispersed in a metallic matrix.

The advantages which powder metallurgy has to offer in nuclear engineering are especially the small grain structure of some of the sintered products and the random distribution of point defects in the crystal lattices. The ability of powder metallurgical products to bond well to other metals is also superior to that of metal made by a more conventional technique—a fact which is of importance with respect to the heat transfer problems occurring in nuclear reactors.

New powder metallurgy methods, such as powder densification by the rolling technique, or metal powder slip casting, offer many advantages in nuclear engineering.

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Discussions

Dr. R. Caillat (*France*) : *Concerning the Sintering of Uranium* : The decomposition of hydride UH_3, cited by the author presents some difficulties: it gives an extremely divided, highly pyrophoric and reactive metal powder whose manipulation is extremely difficult and can scarcely be envisaged in the laboratory. We could judge the reactivity of such uranium powders from the following example; R. Caillat, J. Coriou and P. Perio have stated, by showing the existence of α - variety of hydride UH_3, that the powdered uranium obtained by the decomposition of hydride, of course at low temperatures, reacted with hydrogen even at —80°C.

It is usual, at least in Frnace, and undoubtedly in England, as Mr. Wyatt would confirm it, to prepare uranium powder by reducing UO_2 with calcium or magnesium. It is not sufficient to obtain sintered uranium with fine and disoriented grains. The communication of Mr. Hausner does not mention an important difficulty: the enlargement of the size of grains, after sintering in the course of utilisation. If the grain enlarges, which I fancy, barring special conditions, we are faced, in a general way with the properties and behaviour displayed by cast uranium.

In fact, sintering of uranium was envisaged in the hope that the oxide films at the boundary of grains would prevent their swelling. I do not think that this had been verified, except at low temperatures. With this outlook, we have tried, in France, to envelope the grains of uranium with the carbide UC.

Concerning the Sintering of UO_2 : The behaviour of uranium oxides in the course of their sintering in different atmospheres appears to me far more complex than that presented by Mr. Hausner.

For example, I presume that sintering in an oxidising atmosphere or air is not excluded for UO_2, provided cooling takes place in a neutral or reducing atmosphere. This can even be recommended in certain cases. The importance of the difference in the stoichiometric composition of the oxides and the accelerating effect of humid atmospheres still remain to be mentioned. I do not think moreover, that these different behaviours of uranium oxides are clearly understood.

In conclusion, I would, however, mention that U_3O_8 far from being repeatedly used as raw material for the sintering of UO_2, can on the contrary be recommended highly in certain cases. Thus, we have prepared pellets of sintered UO_2, of diameter 1 cm, height 1 cm, with a density higher than or equal to 10.4 by sintering the compressed pellets of U_3O_8 at 1600°C in an atmosphere of hydrogen.

Author's Reply (*communicated*) : *Concerning the sintering of uranium* : The experiments described in my paper concern the hot

compacting of uranium powder and were made with decomposed uranium hydride. The uranium structure in this way is characertised by randomly fine grains.

Whether these grains will grow or not depends on the processing and operating temperature; for example, uranium powder compacted at 630°C will have grains which grow rather rapidly whereas the same powder compacted at 600°C does not show any grain growth even when heated at 600°C for 700 hrs.

Any hot pressed uranium, whatever the hot pressing temperature, however, will show rapid grain growth if heated above the α to β-transformation temperature.

It is a fact that uranium made by hot pressing shows little ductility in the hot pressed state, but this can be overcome by heat treatment, which does not necessarily result in grain growth.

I never made any experiments myself with uranium power made by the reduction of uranium oxide with calcium or magnesium.

Concerning the sintering of uranium oxide : Sintering of uranium oxide is a complex problem. There are several methods for fabricating uranium oxide particles, and the sinterability of the powder depends strongly on the process of fabrication. (It depends actually on the degree of defectness in the uranium oxide lattice.)

It is my experience that slightly oxidized uranium oxide powders sintered in hydrogen densify faster than powder particles of the precise stoichiometric compound. U_3O_8 powders are in my opinion no desirable raw materials for sintering, mainly on account of the greater shrinkage of the compacts during sintering. I believe strongly, however, that the time will come when we will use not very precisely shaped UO_2 pellets as a reactor fuel. The close tolerances which we apply at present to dimensions of the UO_2 pellets make this fuel extremely expensive and I believe that these tolerances can be considerably adjusted in order to fabricate a less expensive fuel.

Prof. E. I. Mozhukhin, (*USSR*) : Concerning the defects in crystal lattice of the metal powders, the magnitude of internal defects in the crystal lattice is more important than the magnitude of the defects in the surface of the crystals because the number of internal atoms is more than the number of surface atoms. This has been well established in the sintering of iron powders, for example. I think that the same picture would hold in the case of resistance to radiation damage.

Regarding the sintering of uranium oxide compacts in hydrogen or inert atmosphere mentioned by Dr. H. H. Hausner, easily oxidisable powders such as alloys with large amount of aluminium could be sin-

tered under the so called protective vacuum. It is the vacuum where there are only hydrogen or argon molecules in vacuum. Under these conditions the process of oxidation is completely prevented. In ordinary vacuum, however, the process of oxidation takes place during sintering. I am speaking of a vacuum of the order of 1 micron at 1400°C.

Author's reply (*communicated*) : Professor Mozhukhin is correct in stating that the magnitude of internal lattice defects in powder particles is greater than on the surface; however when the particles are very small or agglomerates of very small ones, such as for uranium, surface lattice defects represent a factor which already affects the behaviour of a powder metallurgy product under irradiation. I am of the opinion that metal powders, hot pressed at high pressure and fairly low temperature, still have a large amount of the surface defects present. Sintering at elevated temperature or annealing of hot pressed metals usually decreases considerably the number of defects in the lattice, which then become more "ordered" and this material is then more susceptible to irradiation.'

FUNDAMENTAL CONSIDERATIONS IN THE ALLOYING BEHAVIOUR OF THE HEAVIER METALS

*By J. Friedel**

ABSTRACT

A brief review is made of the various types of bonding which are expected in the alloys of the heavier metals, as regards both intermetallic compounds and primary solid solutions.

It is a very difficult task to speak at this time on the alloying behaviour of the so-called nuclear metals. This is a very new field, of technological importance, and still much unknown or classified. What I would like to point out here, as an outsider, is that, for these metals, the problems should be very much the same as for the more usual metals, if somewhat more complicated. In other words, the fundamental considerations by Hume Rothery[1] should apply. I shall restrict myself to the alloys with the heavier metals (Th, U, Pu), which are especially interesting because of their marked versatility. The structure of these pure metals will be first briefly analyzed.

Structure of the pure heavier metals (Th, U, Pu)

It is of course useful to try and have some clear picture of the structure of these metals when pure, before studying their alloys. In the last series of the periodic table, the 5 f character should predominate more and more over the 6 d one with increasing atomic numbers. This point seems related to the structures observed.

Atomic structures : As can be seen in fig. 1 and 2, the structures observed for these metals can be classified in three groups :

A : In these metals with a relatively small number of valence electrons per atom, the fairly compact structures observed are nearly those observed at the beginning of a *transitional* series like that for Rb to Ag for instance: FCC, BCC and, for Pa, a body centred tetragonal very near to a BCC. Up to Pa, the stability, measured for instance by the melting point T_m increases regularly with the atomic number N. The atomic radius, measured for instance by the radius of the atomic sphere (i.e. $\frac{4\pi r_S^3}{3}$ = the volume per atom§), decreases regularly with

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§ This is probably the best definition for the atomic size in a metal, as it is usually very insensitive to allotropic transformations.

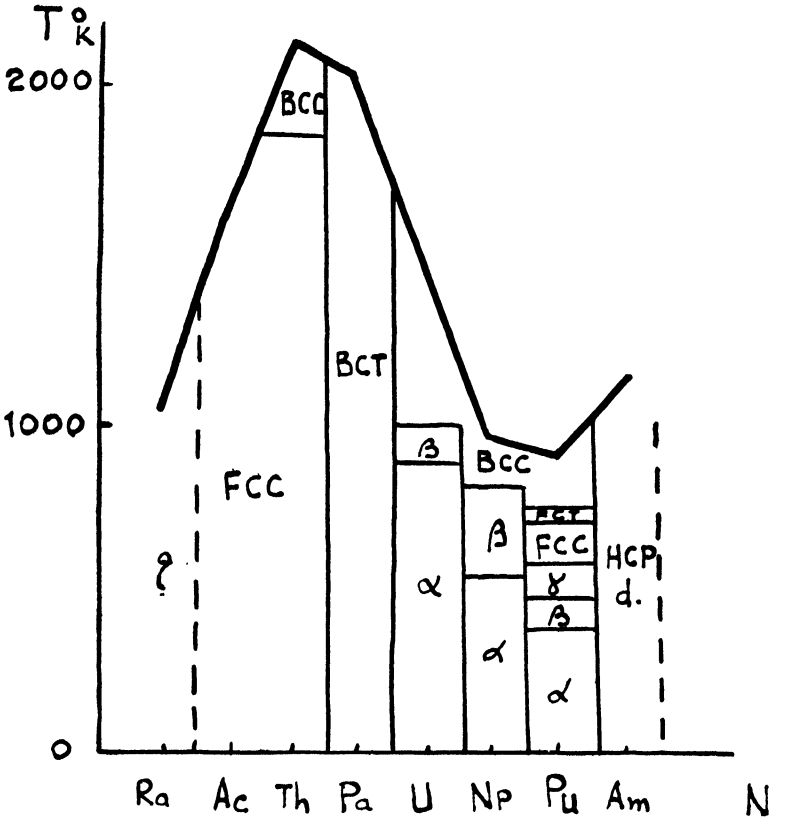

Figure 1.—Melting points T_m versus the atomic number N for the heavy metals α, β ə γ are complex structures.

increasing N(fig. 3). These variations of T_m and r_s are very similar to those at the beginning of a transitional series.

B : The low temperature phases α of U; α and β of Np; α β, and γ of Pu are very complex and far from close packed, each atom being surrounded by a small number of neighbours, with whom they seem to build up directed *covalent bonds*. These bonds have an *unsymmetrical* distribution around each atom. Fig. 4 represents the simplest of those structures, that of α -U, where each atom has four unsymmetrical bonds AB, AC, AD, AE. The number of allotropic transformations and the low melting points show that none of these phases is very stable, contrary to the corresponding transitional elements. It must be stressed however that, for a given metal, the densities, thus the atomic radii, of these phases are very similar to each other and to that of the high temperature BCC phase.

C : Am has a 'double' HCP structure which is observed other wise only in some *rare earth metals*. It might be thought that the FCC δ and

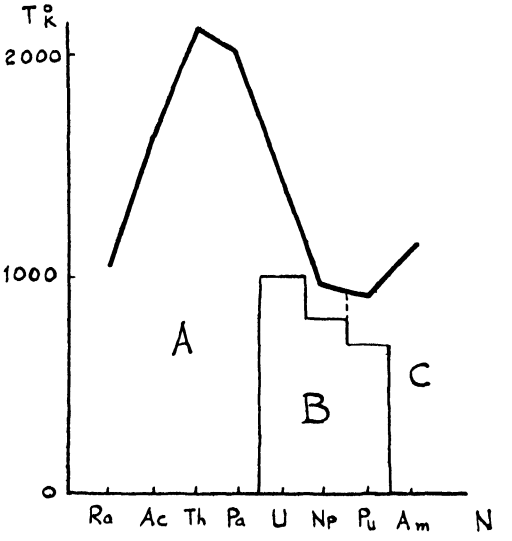

Figure 2.—The three regions A, B, C for the heavy metals

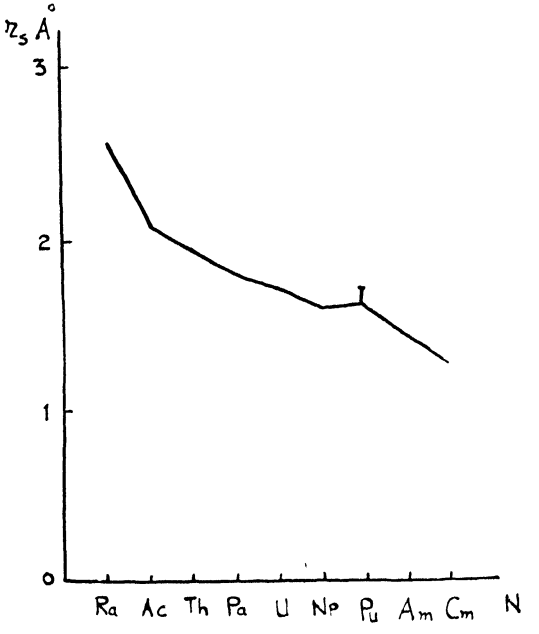

Figure 3.—Atomic radii r_s versus the atomic number N for the heavy metals

related δ′ phases of Pu, with an anomalously low density, perhaps correspond to the structure of rare earth metals. The BCC structure observed at high temperatures in Pu, and the low melting points are also features of rare earth metals.

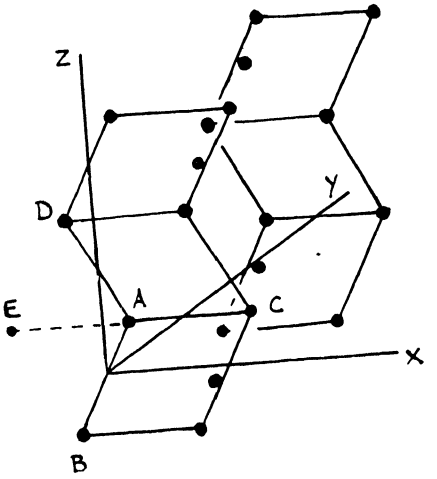

Figure 4.—Atomic structure of ∝ -uranium

Electronic structure : Th, U and Pu are known to have a *large density of* states n at the Fermi level E_m This is shown both by their large electronic specific heat $\triangle C\nu = \nu T$ and their large and fairly temperature independent paramagnetic susceptibility χ (fig. 5). As in the usual transitional metals, this can be interpreted as showing that the band approximation applies; and that a fairly *narrow band,*

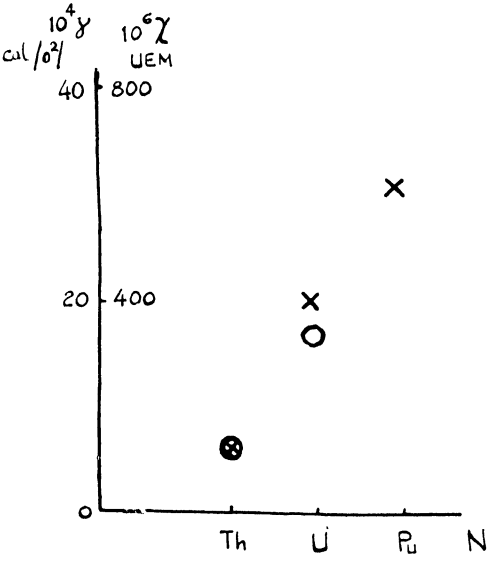

Figure 5.—Density of states at the Fermi level, deduced from the electronic specific heat $\triangle C\upsilon = \gamma T$ and from the magnetic susceptibility× .Crosses : ⟩ in 10^6UEuCm^{-3} circles : in 10^4 cal deg $^{-2}$ mole^{-1} < 1.

deduced mainly from fairly localized atomic levels, *overlaps the Fermi level*[2]. Phonon induced transitions from the usual conduction band to this narrow band explain the high electrical and thermal resistivities observed. The fact that the atomic radius r_s of such metals are little affected by allotropic transformations or melting also points out to a strong metallic character: easily excited, and thus fairly free, electrons are more sensitive to changes of volume than to shears.

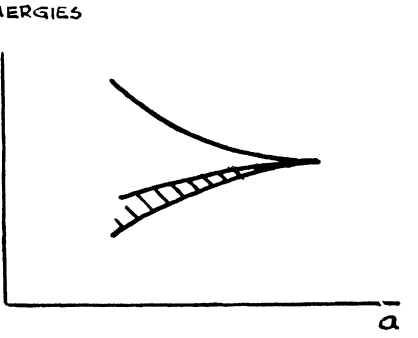

Figure 6.—Broadening of the d levels into a band, when the interatomic distance a decreases (schematic).

The three groups A, B, C have distinctive characters :

In group A, as at the beginning of any *transitional series,* the increasing stability may be explained by the progressive filling of a ds *band* which should still be fairly broad in the energies*. This is in agreement with the compact atomic structures observed, characteristic of fairly free electrons, and with the still not too large density of states n (E_m) observed for Th. The body centered cubic or tetragonal structures of Th, Pa and U recall similar ones observed in the transitional elements of the same columns (Zr, Nb, Mo for instance). As in these metals, it may be stabilized by some covalent character in the d band, which would tend to split it into a 'bonding' and an 'antibonding' part. Thus the physical properties of BCC U sugest the band structure pictured in fig. 7 a: part of the 6d band, corresponding roughly to covalent bonds between nearest neighbours, would have an especially low energy[3]. The β phase of uranium is the same as the σ phase observed in many transitional alloys. It should thus be connected with same bonding through d electrons.

The characteristic structures observed in group B are probably due to the appearance of a notable 5 f character in the narrow bands overlapping the Fermi level[3]. It is easily seen that hybridization by such an atomic function should lead to covalent bands both *assymmetrical and complex.* The physical properties of U α for instance suggest the

* One can reasonably assume the d atomic levels to be broadened into a band with the same average energy, as pictured in fig. 6. The cohesive energy should therefore be of the order of the number of d electrons times about half the width w of the d band. This gives for Th w $\simeq$ 5 to 7 e.V. assuming two 6d electrons per atom.

band structure pictured in fig. 7 b, with a full and narrow 6 d-5 f band, containing 4 electrons per atom and corresponding to the 4 covalent bands pictured in fig. 4. This 'bonding' band would be much less stable than that in BCC Uranium. Its emptying by thermal agitation would require only 0.2 to 0.3 e.V; the corresponding breaking of covalent bonds explains probably the anomalies observed in this phase at high temperatures.

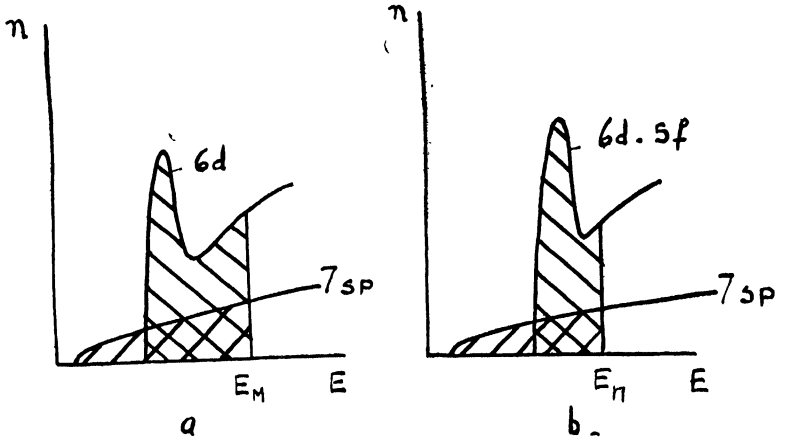

Figure 7.—Proposed band structure for uranium. a : γ phase ; b : α phase

If the structures in group C are really like those of rare earth metals, some at least of their electrons should be in *atomic* 5 f *orbitals* which are too localized to build up a band. Each atomic shell should have, from Hund's rule, the maximum possible magnetic moment, oriented, at random, independently from its neighbours at high temperatures. This should lead to a Langevin paramagnetism, with a susceptibility χ decreasing inversely with temperature[4]. No measurement has been made so far on Am. In the high temperature phases of Pu, χ decreases rather slowly with increasing T, and has values not much larger than those for the low temperature phases. Thus, in these metals, even if there are independent 5 f shells, there are probably also electrons in a narrow 6 d band overlapping the Fermi level. Finally, it may be pointed out that the high temperature phases of Pu have much larger atomic radii than the low temperature ones. This behaviour is very unusual for a metal. It suggests a strong difference in electronic structure, and certainly would stabilize atomic 5 f shells in the high temperature phases.

In conclusion, the atomic structure and physical properties of these metals may be understood by an increase of 5 f character with respect to 6 d character as the atomic number increases. Thus the series starts like that of an ordinary *transitional* series, with a fairly broad 6 d band (region A); then an increasingly large 5 f hybridization of the 6 d bands leads to *complex and assymmetrical covalent structures* (region B); finally the 5 f atomic shells may become stable and loca-

lized enough on each atom to have a spontaneous magnetization, independant from that of its neighbours, like in *rare earth metals* (region C?).

Intermetallic compounds

There is much evidence that most of the general considerations developed by Hume-Rothery[1] apply to the intermetallic compounds formed by the heavier metals with other elements. We shall briefly review the possible importance of the size, electrochemical and valency factors.

Size factor : Th, U and Pu form a great number of ordered compounds where the size factor seems important. For instance one observes many Laves phases AB_2 with atomic radii r_{SA}/r_{SB} between 1.2 and 1.3, as required[1].

This is shown in the next table.

Laves Phases

Alloy (Cu_2Mg type)	r_{SA}/r_{SB}	Alloy (UCu_5 type)	r_{SA}/r_{SB}
UAl_2	1.09		
UMn_2	1.20	UNi_5	1.24
UFe_2	1.22	UCu_5	1.21
UCo_2	1.24		
$PuAl_2$	1.14	Alloy (MgZn type)	r_{SA}/r_{SB}
$PuMn_2$	1.26		
$PuFe_2$	1.28	UNi_2	1.24
$PuCo_2$	1.30	$ThMn_2$	1.39
$PuNi_2$	1.30	$Pu\ Os_2$	1.21
$PuRn_2$	1.22		

The atomic radius for Pu has been taken as that for the high temperature cubic phases.

Similarly, metals with comparable radii tend to form an ordered $AuCu_3$ type of structure. This is shown in the next table, where $\epsilon = \frac{2(r_{SA} - r_{SB})}{r_{SA} + r_{SB}}$ is the size factor ($\epsilon = 0.12$ for $Aucu_3$)

$AuCu_3$ type of structures

Alloy	Size factor
UAl_3	0.08
UGa_3	0.02
UPb_3	0.12
USi_3	0.02
USn_3	0.08

It must be emphasized that the size factor is *not* the only stabilizing factor in these compounds. It allows the atoms to find their place in these compounds, thus suppressing the elastic distortions which would occur from their difference in size in a random solid solution. Now, in a liquid alloy, most of the elastic distorsions are also known to disappear[5]. Thus the melting point T_m of the compound should be depressed, with respect to the average melting point of the alloy, by the entropy of disorder in the liquid alloy. It T_A and T_B are the melting points of A and B, C_A the concentration in A, one finds by equating the free energies of the concentration in A,

$$T_m - C_A T_A - (1-C_A) T_B \backsimeq T_m [C_A \log C_A + (1-C_A) \log (1-C_A)] = - \propto T_m \ldots\ldots\ldots (1)$$

where $\propto$ is a positive constant of the order of $\frac{1}{2}$. Experimentally, the depression of T_m with respect to T_A and T_B is much smaller than that predicted by (1). This can mean that the entropy of disorder in the liquid is much smaller than the random entropy assumed in equation. (1); or, more probably, that there is a further electrochemical factor which somewhat stabilizes the alloy when in the ordered structure of the compound.

Electrochemical factor : From the discussion of § 1, Th, U and Pu have probably electro-negativities comparable with those of the rare earth metals and the metals at the beginning of a transitional series (x=1 to 1.5 on Pauling's electronegativity scale[6]). They should therefore make strong *ionic compounds* with all the markedly electronegative elements (x>2, thus C, N, O, F; S, Cl; Se, Br; Te, I). H, B, P, As, Sb and Bi should be on the borderline. Many fairly stable compounds with obviously ionic character are indeed observed. Thus for instance the NaCl type of structure is observed for the following compounds

Alloys with NaCl Structure	T_m °K
UC ..	2470
ThSe ..	2020
Pu Bi ..	>1700
PuO ..	2700

A measure of their heats of formation would indicate the strength of their ionic character. Their high melting points (T_m=1080 for NaCl) show that it is certainly strong.

With more electropositive metals, Th, U and Pu can perhaps make ordered compounds where the Madelung energy is still significant. *This energy should however be usually very small.* For let us con-

sider two metals A and B with same atomic structure and the same atomic size, but different Fermi energies E_A and E_B. When mixed together, the electrons in the atoms with the higher Fermi energy, say A, will tend to overflow to the neighbouring atoms B, until the dipole layers thus created at the limits between these atoms just compensate the difference in Fermi energies $E_A - E_B$. The Madelung energy stabilizing an ordered AB structure will be proportional to the square of the charge Q thus given by an A atom to a B one[2]. Now, from a general Thomas Fermi argument, it can be shown that the width q^{-1} of the dipole layers should be given, in atomic units $e=m=n=1$, by

$$q^2 = 4\pi n(E_m)^{2\eta} \quad \ldots\ldots\ldots (2)$$

where $n(E_m)$ is the density of states at the Fermi limit in the alloy. and that

$$Q \leq \frac{\text{const } a^2}{q^3}(E - E_B) \qquad (3)$$

where the constant is of the order of unity and a is the interatomic distance.

From the discussion of § 1, it is self-evident that q^{-1} will be small, especially for alloys with normal transitional metals. The charge Q and the Madelung stabilizing energy will correspondingly be much smaller than in alloys between 'normal' metals with the same difference $E_A - E_B$ in electronegativity.

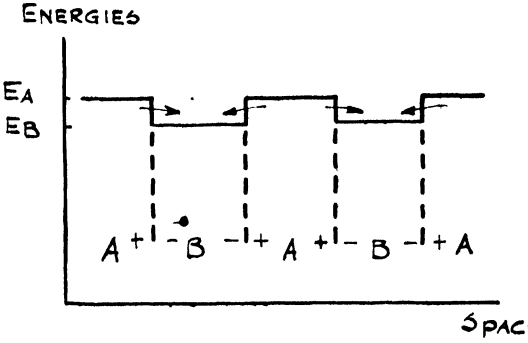

Figure 8.—Electronic rearrangement, due to a difference in electronegativity, in an intermetallic compound

Valency factor: The so-called *Hume-Rothery compounds* observed in 'normal' alloys, such as the β brass CuZn, do *not* seem to exist with the heavy metals. These compounds are characterized by their occurrence near to definite numbers of valence electrons per atom, by their fairly large ranges of compositions, and by their small stability with respect to each other and to the primary solid solutions; many of them are furthermore very complex in structure and often disordered. Except for a very few cases such as the very broad and ξ phases of UPu, the compounds formed with the heavy metals are, on

the contrary, occurring at very definite and often simple compositions. Except again for a few cases such as these phases or also UBi, their structures are usually very simple. Finally they are usually stable enough to restrict severely the range of primary solid solutions.

This absence of proper Hume Rothery compounds is of course to be expected from the fact that the valence electrons of the heavy metals are far from free. Compounds preserving the *covalent bindings* of these metals are more likely to be observed. The η and ξ phases of UPu thus probably preserve some kind of 5 f-6d covalent bonds. Some of the BCC and BC tetragonal phases observed with transitional metals probably preserve the covalent 6 d bands towards nearest neighbours. No systematic study of these cases exists so far.

Primary solid solutions

When defining the solubility of a solute element into a solvent, one has to fix its ranges of solubility in the various allotropic phases and also its effect on the allotropic transformations. These points will be summarily dealt with.

Effect of alloying on allotropic transformations: General equations; We want to know how the solution of element A alters the allotropic transformation α to β of element B. Let $C\alpha$, $C\beta$ be the atomic concentrations in A of the α and β phases in equilibrium at temperature T (fig. 9). For small enough concentrations $C\alpha$, $C\beta$, the atoms of A

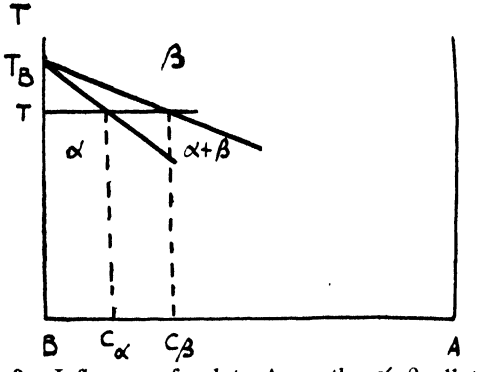

Figure 9.—Influence of solute A on the α β allotropic transformation of solvent B.

are certainly at random. Thus the free energies of the two phases at temperature T may be written

$$F_\alpha = C_\alpha (U_{A\alpha} - TS_{A\alpha}) + (1-C_\alpha)(U_{B\alpha} - TS_{B\alpha}) \ldots\ldots (4)$$
$$+ \Delta F_\alpha (C_\alpha) + KT[C_\alpha \ln \eta\ C_\alpha + (1-C_\alpha) \ln \eta (1-C_\alpha)]$$
$$F_\beta = C_\beta (U_{A\beta} - TS_{A\beta}) + (1-C_\beta)(U_{B\beta} - TS_{B\beta}) + \Delta F_B\ (C_\beta) \ldots (5)$$
$$+ KT\ [C_\beta \ln \eta\ C_\beta + (1-C_\beta \ln \eta\ 1-C_\beta)]$$

In these expressions, we have introduced the energies U and entropies S of the two pure elements in the two phases, and also the parts Δ F of the *free energies of formation* which do not contain positional entropies. Thus the Δ F's contain the internal energies and vibrational entropies of formation of the alloys. They are counted *per atom of alloy,* thus tend to zero for c→o or 1.

The equilibrium of the two phases is obtained by writing

$$\frac{F_\alpha - F_\beta}{C_\alpha - C_\beta} = \frac{d F_\alpha}{d c_\alpha} = \frac{d F_\beta}{d c_\beta} \qquad \ldots\ldots\ldots\ldots (6)$$

One can assume the U's ans S's to be temperature independent and introduce the temperatures of transformation T_A and T_B and the heats of transformation :

$$L_A = U_{\beta A} - U_{\alpha A} = T_A (S_{A\beta} - S_{A\alpha}) \qquad \ldots\ldots (7)$$

$$L_B = U_{B\beta} - U_{B\alpha} = T_B (S_{B\beta} - S_{B\alpha}) \qquad \ldots\ldots\ldots (8)$$

The equations (6) then give, for T→T_B, the well known relations

$$kT_B (c_\beta - c_\alpha) = L_B \left(1 - \frac{T}{TB}\right) \qquad \ldots\ldots\ldots (9)$$

and

$$kT_B \ln \frac{c_\beta}{c_\alpha} = L_A\left(\frac{T_B}{T_A} - 1\right) - \left[\frac{d}{dc}\left(\Delta F_\beta - \Delta F_\alpha\right)\right]_{c=0} \qquad (10)$$

The derivative $\left(\frac{d\ \Delta F}{dc}\right)$ c = 0 are the 'free energies of dissolution' of A in pure B, counted per A atom and in a given phase, α or β. In some cases, it is more interesting to introduce the free energies of dissolution of A in pure B, taking A always from the *same* phase (α, or β, or the vapour, etc..). Denoting these free energies by f_α and f_β, one has of course

$$kT_B \ln \frac{c_\beta}{c_\alpha} = f_\alpha - f_\beta \qquad \ldots\ldots\ldots\ldots (11)$$

Melting. Size effects : Equations (9) and (10) can be used to study the slopes, for small concentrations, of the solidus and liquidus in a solid solution BA*. For solid solutions with fairly close packed structures, as is usually the case here, melting occurs without much change in density or in the average number of neighbours around each atom. The electronic structure should therefore be little affected, ex-

* BA means A dissolved into B.

cept for a certain 'fuzziness' of the limits of the energy bands. This would be important only for Hume—Rothery types of alloys, which, as pointed out above, do not seem to exist. The main change occurring by melting is therefore the destruction of a regular lattice, which allows each atom to find more easily a place suited to its size, thus reduces considerably the elastic energy due to the size effect. Thus, in equation (10), we can write

$$\left[\frac{d}{dc}\left(\Delta F_{\beta} - \Delta F_{\alpha}\right)\right]_{c=0} \simeq \omega \qquad \ldots\ldots\ldots\ldots (12)$$

if α is the solid and β the liquid phase. ω is the strain energy per A atom, approximately given by

$$\omega \simeq 3\,\mu\, r_S^3\, \epsilon^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots (13)$$

if μ is the shear modulus of the matrix[5].

The following table shows that the values of ω deduced from the behaviour of the solidus and liquidus, by equations (9), (10) and (12), agree reasonably well with the theoretical values (13) (energies in e.V. per atom), in copper base alloys. In equation (10), the values L_A, T_A for the pure solute element in its stable structure have been used, instead of the (unknown) values for the FCC structure. The difference should be slight, except for elements like Ge where the FCC structure would surely be very different from the observed diamond structure.

Alloy	C_L/C_S	ω mes[12]	ω theor[13]
Cu Zn	1,25	0.08	0.07
— Ga	1,9	0.25	0.30
Ge	3	0.15	1.0
As	6	0.2	0.3

It would be interesting to check the validity of this approach in solutions with the heavy metals. Unfortunately, the positions of the liquidus and solidus are usually too much uncertain for this. It is easily checked for instance that the published diagrams lead, by applying equation (9), to heats of melting of U which vary by a factor 2. We shall therefore describe only qualitatively what is expected, depending on whether ω is large or not. We shall assume for simplicity that

$$L_A \simeq kT_A \text{ and } L_B = kT_B$$

a.—Small size effect: $\omega \simeq 0$ (e.g. UZr). L, and S should vary regularly from T_A to T_B (if there are no intermediary compounds), as pictured in fig 10. For temperature T near to T_B, one should have

$$\frac{NP}{ON} = \frac{NM}{ON} = \frac{[T_A - T_B]}{2\,T_A}$$

b.—Large size effect: $\alpha = \propto$ (e.g. UTh). S should be practically vertical, and L should extrapolate to 0°K at the other end of the diagram, as pictured in fig. 11 : $C_L = 1 - T/T_B$

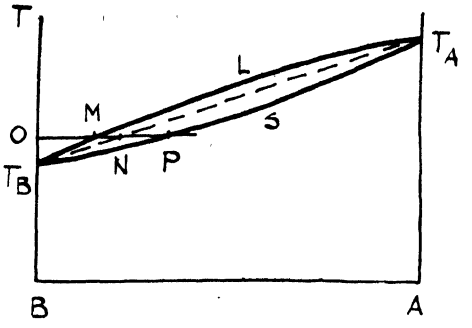

Figure 10.—Liquidus L and solidus S for no size effect

c.—Medium size effect: (e.g. ThZr). L and S should be somewhat depressed in the centre of the diagrams, as shown in fig. 12. The general relations above should then be used. As a useful order of magnitude, $C_L/C_S \leq 10$ for a size factor $\epsilon = 15\%$.

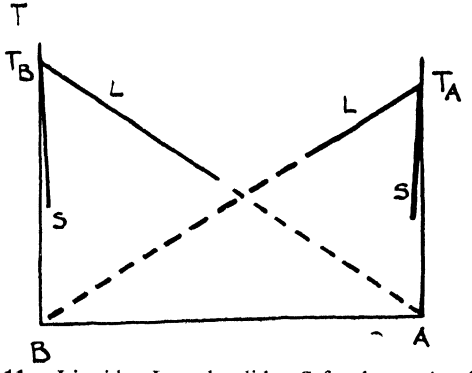

Figure 11.—Liquidus L and solidus S for large size factors

Solid phases. Valency effects : Here too, equation (9) is very poorly obeyed by the published diagrams, so that only qualitative discussion is possible.

For *substitutional* alloys, a *valency* effect is well known for the $\alpha \longrightarrow \gamma$ transition of iron. In that case, the heat $Q_B = kT_B \ln \frac{C_\gamma}{C_\alpha}$ figuring in equations (10) or (11) seems to vary roughly as the difference of valencies of the solute and solvent metals[7]. Dwight[8] has recently pointed out that a similar law seems to hold for the $\alpha\beta$ and $\beta\gamma$ transitions of uranium. No simple explanation of this fact has been found so far.

For *interstitial* alloys, one might think that the size effect is predominant. The difference $f\alpha - f\beta$ in the energies of dissolution of B in A should then be mainly due to the difference in strain energy. The α-phase should thus be stabilized with respect to the β-one if it offers larger interestitial holes or is elastically softer than β (and conversely). In uranium for instance, the strongly covalent α-and β-structures are more open than the BCC γ-structure. They are thus stabilized by adding interstitial silicon.

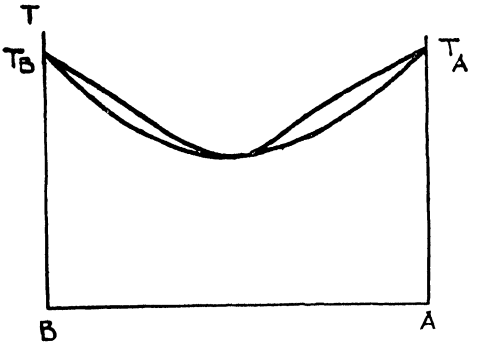

Figure 12.—Liquidus L and solidus S for intermediary size factors

Range of solubility : This is a much harder problem to solve, because it involves the relative stability of a primary solid solution with respect to intermediary compounds or to the other primary solid solutions. The general Hume-Rothery rules seem to apply. Thus a large range of solubility requires :

a—a small size factor ($\epsilon << 15\%$). Thus only elements of the rare earth series or of the 4th to 6th columns in the transitional series (e.g., Zr to Mo), or elements at the end of the transitional series (e.g., Pd to Cd) can dissolve appreciably in U, Pu or Th. Pu dissolves more easily than U in Th because of the versatility of its atomic radius.

b—a small electrochemical factor. This point is less clearly defined. But the much smaller solubilities of the 4th to 6th columns in the third transitional series is surely connected with the existence of the 4 f shells which gives to this series a comparatively larger electronegativity. This stabilizes the intermediary compounds with respect to the primary solutions.

c—valency effects of the Hume-Rothery type are unknown for primary solutions as well as for intermetallic compounds. The same reason holds: the valence electrons are far from free. It is certain however that the elements which dissolve best are those with similar electronic structures: d bands with similar structures in BCC alloys of the heavy metals with the transitional elements of the fourth to the sixth periods; U and Pu together in all their phases etc. . . . The large solubility of U in Pd is certainly connected with the filling of the d band of Pd by

the valence electrons of U, although the primary solution extends somewhat further than the filling of that band[9]. Much more experimental work on the physical properties of these solutions would be required to understand fully their stability. This would certainly also throw a light on the electronic structure of the pure metals.

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PREPARATION OF RARE EARTH METALS

By Felix Trombe *

The preparation of rare earth metals is a difficult operation, particularly if we want to obtain them in the pure state. In fact, these metals are very electropositive; most often, they combine or alloy, with large evolution of heat, with almost all elements except the rare gases. The difficulty of preparation of rare earth metals is further increased by the fact that they are rather refractory, this property increasing with the atomic number cerium melts at about 800°C whereas lutecium melts at 1700°C.

Another aspect of the question, which complicates the metallurgy of rare earths, is that of the quantity of matter which can possibly be treated. It is known that, among the elements of rare earths, those, which possess even atomic numbers are more abundant than their neighbours with odd atomic numbers. The content of different rare earths in an ore is therefore represented, as a function of atomic number, by a serrated curve, but this curve will be, according to the ores, upwards or downwards.

The ores with downward curve, of monazite type, will be deficient in heavy earths. The ores with upward curve, of xenotite type, will be rich in heavy earths. Unfortunately, the latter ores themselves are relatively rare whereas monazites, for example, are very abundant.

A general statistics on rare earth ores, a statistics combining the relative proportions of ores in the terrestrial crust and their content of different elements, gives a downdard curve; cerium, for example, is a relatively abundant element in the terrestrial crust; it is less rare, in lithosphere, than Cu, Zn, Pb, or Sn. The heavy elements, on the contrary, are much rarer, especially, as we have said, the odd elements. Europium, terbium, holmium, lutecium are the rarest.

Yet another aspect of the question is that of separations of elements among themselves. Cerium is separated with ease chemically; some others, like samarium, europium, ytterbium are also separated chemically but, for many others, and particularly, terbium, holmium, lutecium, the odd elements, the separation, even by modern methods, is laborious.

From all this, it follows that metallurgical operations, which can be carried out, if we so desire, on tons of cerium, should necessarily be employed, for the rarest elements, on small quantities of matter. The

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ratio of the surface of the crucible in which the metallurgy is effected and the volume of matter which is in contact with it, is necessarily large (let us recall that the value of this ratio is proportional to the diameter of the crucible). It follows that a small quantity of metal is in contact with a large surface of the crucible and can easily take in it its impurities or act on the material which constitutes it. This case is particularly unfavourable for the production of a pure metal.

It is particularly difficult to find crucible material which can contain both the metals in the molten state as also the conducting substance, unattackable by them, which could eventually be useful for their electrolytic deposition.

In the class of substances, which are nonconductors of electricity, certain refractory oxides with very large heat of formation, like beryllia, magnesia or lime, or a mixture of these two latter oxides arising from the calcination of dolomite, resist well the action of rare metals at high temperature. Nevertheless, we observe an equilibrium reaction between the rare metals and these oxides, such as, for example, a fusion in magnesite crucible leads always to a rare metal containing 1 to 2 parts per thousand Mg. This same phenomenon, in a more accentuated form, is observed with oxides having equally large heat of formation, like thoria, zirconia, and alumina. Silica, which should be attacked more than the 3 previous oxides, is less attacked and has been used for preparing rare metals containing a thousandth to a few thousandths part of silicon.

A compound which seems to resist the action of rare metals very well is CaF_2 (1). Metallic cerium may be melted without introducing calcium in it. Its principal defect is its relatively low melting point (1360°C), lower than the melting points of most of the metals of the yttrium group. On the contrary, it will be very useful for the preparation of fusible alloys (4), serving eventually as intermediary stage in the isolation of rare metals.

Among the conductors of electricity, we will retain, in view of the previous usage, C, Mo (1—2) ; W and Ta. Carbon can be used as an anode during the electrolysis of fused rare earth salts; it can also be used as crucible for the rapid fusion of certain metals of the cerium group (cerium, lanthanum, praseodymium) without carbonizing them in an appreciable manner.

Tungsten, and particularly molybdenum, have been used in recent years as cathode or as lining of crucibles in contact with molten metals. Mo resists better than W at 1100°C, but, at higher temperature, say at 1500-1600°, the attack of Mo becomes important whereas that of tungsten still remains relatively low. For example, a

molybdenum sheet is really corroded by the vapours of rare earth metals at 1600°, whereas lanthanum contained in a tungsten crucible can be distilled (1, 3) at 1700°. This result is probably due to the fact that tungsten is much more refractory (M.P. 3400°) than molybdenum (M.P. 2500°). At present, the alloys of these metals with rare earth metals are not known ; but it is true that the compounds formed are more refractory in the case of tungsten than in that of molybdenum.

The use of tantalum, a metal which is easier to handle and fuse than tungsten and molybdenum, has been recently recommended by Spedding in U. S. A. It has permitted the preparations of pure cerium metal (4) and also those of yttrium group metals. Nevertheless, when we exceed temperatures of the order of 1300°C, it becomes more and more attackable by the molten or vapour-state rare metals.

When, in 1930, under the inspiration of Georges Urbain, the isolation of highly pure rare earth metals was undertaken in France, the properties of pure metals were hardly known.

Recent techniques permitted the isolation of cerium and of several cerium group metals with only a few thousandth parts of impurities. Other methods resulted in the isolation of gadolinium (1934), europium (1938) and dysprosium (1945), and in the preparation of yttrium. It is on these metals that the following properties were discovered, and our knowledge clarified :

(a) the allotropic states of cerium, characterised by magnetic and electrical anomalies and large dilatometric anomalies (1934-1945),

(b) the ferromagnetism of gadolinium (1934),

(c) the ferromagnetism and antiferromagnetism of dysprosium (1945-1953).

Since 1945, the efforts of the American School, under the guidance of Spedding, led to new methods of preparation and elaboration of cerium metals, and almost all the yttrium metals. Now, a large number of new physical properties of rare metals are being determined.

Let us now review the methods of preparation :

Action of hydrogen :

The action of hydrogen on oxides or halogen compounds does not lead to the metal. We obtain a partial reduction of trivalent chlorides of samarium, europium, ytterbium with the formation of divalent chlorides (5). In presence of gold, we can obtain alloys (5).

Action of carbon :

The action of carbon on compounds presenting only a trivalent character leads to stable carbides, generally of the type MC_2, and also, probably to compounds corresponding to other formulae. We shall see, in connection with the preparations by displacement with elimination of rare element by distillation, that we obtain metals when carbon acts at high temperature on oxides of elements having a divalent character—samarium, europium, ytterbium (6) (7).

Electrolytic methods.

(A) **Electrolysis at ordinary temperature :**

The electrolysis of rare earth salts in aqueous medium does not give any appreciable result because the nascent metal deposited at the cathode reacts with water to give the oxide. With a Hg-cathode, we obtain extremely dilute amalgams which react rapidly with water. Better results have been obtained by Audrieth and his collaborators by electrolysis of alcoholic solutions of anhydrous chlorides (8) (9) (10). The Hg contains 1 to 3 % of the rare earth metal. Its distillation would give the pure metal.

The use of Hg as solvent for rare earth metals has been applied by previous authors in the purification of the latter from the crude state. Samarium would thus be separated from its carbide and cerium from iron. Let us also point out a work of Derge and Martin (11) on rare earth metal amalgams. These authors did not obtain the elimination of Hg at 1000°C.

(B) **Electrolysis of fused salts :**

In 1875, Hillebrand and Norton (2) were the first to apply the electrolytic method in the preparation of rare earth metals.

The electrolytic method was taken up by Muthmann with different coworkers between 1902 and 1907 (13) (14) (15). He succeeded in preparing all the metals of cerium group (Ce, La, Pr, Ne, Sm) by electrolysis of fused chlorides contained in a copper water-jacket, cooled by a current of water (Diagram 1).

The anode and cathode are made of carbon. The metals are slightly carbonized, but they are also contaminated by the adjacent rare earths, the initial raw materials employed by Muthmann being not sufficiently pure.

Let us also cite the preparations of Hirsch (1911) (16) and Thompson (1917) (17) who obtained large quantities of cerium in an iron vessel. These were industrial preparations carried out with good

yields by the treatment of technical raw materials. Hirsch also used amalgamation for separating cerium from its impurities.

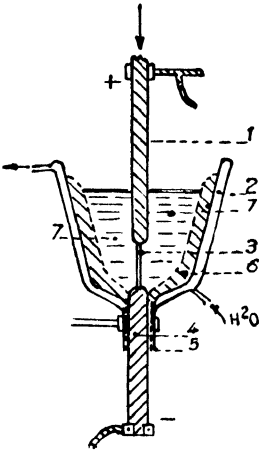

Diagram 1.

In 1925, Kremers, with different collaborators (18), then Schumaker, with Lucas (19) and Harris (20) prepared cerium, lanthanum, neodymium, praseodymium and samarium in a carbon vessel. Kremers and Stevens (21) used a tungsten cathode for the deposition of metal.

In 1930, George Urbain decided to undertake a general study in his laboratory to obtain a sufficiently pure metal starting from rare earth salts of highly controlled purity so that its principal properties could be determined. As he was concerned with operation on pure materials, there was no question of treating large quantities of raw materials.

The preparation of pure cerium, lanthanum and neodymium was done by electrolytic decomposition of their fused anhydrous chlorides with the aid of a carbon anode and a molybdenum cathode. The electrolytic bath (Diagram 2) (1) consists of a purified carbon crucible (LL) serving as anode, a jacket (III) and a porcelain crucible of fluorspar (23) and a molybdenum anode (IV). Thus we have a cathode chamber where the metal is deposited in (X) and an anode chamber where chlorine is set free in (VI). The anode and its protecting jacket rotate at about one turn per second in order to avoid adhesion of metallic particles between anode and cathode. The bath level, maintained in (V), provides a large anode surface and consequently, a low overvoltage on the latter, which suppresses the extremely troublesome classical effect of anodic polarisation.

Besides, the cathodic density is very high, of the order of a few amperes per cm^2, so that a good localisation of metal is obtained. By

virtue of the low energy brought about by the electrolytic current, it is necessary to maintain the temperature of the whole assembly, measured in (VIII), with the aid of external heating (I).

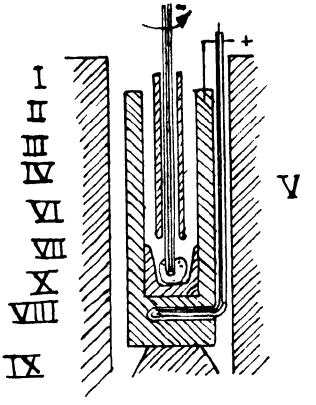

Diagram 2.

Cerium, lanthanum and neodymium thus obtained do not give in the arc spectra any calcium bands and they do not contain molybdenum either. The insolubility of molybdenum in rare earth metals "at red heat" had already been established by Guertler (22).

The defect of fluorspar is its low melting point (1360°) and even in the preparation of neodymium, the dissolution of fluorspar in the bath of fused chlorides becomes very high and renders the latter viscous; the yields of metal are poor. For certain preparations, we have replaced fluorspar by a quartz tube and crucible. The silicon concentration of the metals obtained is of the order of 0.5%, but the yield of metal is evidently higher than that which is obtained with fluorspar porcelain.

The metals obtained by this first method were fairly pure so that we could study some of their physical properties. In particular, the preparation in fluorspar porcelain permitted to have metal concentrations of the order of 99.8%, after a refusion under vacuum, meant to eliminate alkaline earth metals which exist in small amounts after cooling in the rare metals prepared.

A few attempts of direct electrolytic deposition of yttrium metals from their fused salts have shown that, in the group of rare earths, the melting point of metals, except for a few inversions, increased with atomic number. It became difficult, particularly for yttrium metals, to carry out electrolysis at suitable temperatures so that the metal was deposited in the fused state and, at the same time, the halogenated compound submitted to electrolysis did not volatilise. Moreover, the

choice of refractory materials resisting at the same time the attack of molten bath and metal was found to be equally difficult.

It is also in the laboratory of Georges Urbain (1) that a method of preparation of rare earths was evolved to overcome the previously mentioned difficulties. The principle of this new method consists in transposing to the domain of fused electrolysis the techniques which give amalgams in aqueous electrolysis.

We have seen that the amalgams of rare earths are of very low concentrations, at the ordinary temperature, and the low boiling point of Hg (360° under 760 mm) does not permit its use at high temperature in presence of fused salts.

The classical Hg-cathode has been substituted by a fused cathode of Cd or Zn and the aqueous solution by a molten mixture of the chlorides of rare earths and an eutectic of alkali chlorides of KCl and NaCl. Cd (M.P. 320°, B.P. 775°) and Zn (M.P. 419°, B.P. 920°) appeared, a priori, to be convenient for the previous operation. The electrolytic arrangement is the same as that described previously and shown in Diagram 2, with the only difference that the largest part of the lower crucible (VII) was occupied, from the beginning of electrolysis, by a molten bath of one of the previous metals. It is thus that the different alloys of Cd and Zn with rare earth metals have been obtained. These alloys, easy to separate from the bath of fused salts, are later cleaned on the surface and submitted to a distillation under vacuum, at high temperature, which eliminates by volatilisation, the metal from the cathode leaving the rare metal in a pure state. The concentration of alloys can vary from 4 to 25% according to experimental conditions.

By this process, after conclusive preliminary experiments on the preparation of La and Sm, Gd (1934) (1) (24), Eu (1938) (25) and Dy (1945) (26) have been isolated from their alloys with Cd.

Scandium has been obtained by the same method from its alloy with zinc (27).

The previous method gives good yields according to the electrolytic operation and permits, while operating with small quantities, to collect the rare earth metal into a compact alloy which can easily be cleared from chloride. It has been verified, particularly for alloys with Cd, that there does not remain practically any solvent metals in the rare earth metal after treatment under vacuum.

Methods of preparation by displacement

Numerous attempts have been made to displace rare earth metals from their salts or from their oxides.

Generally, an element capable of giving an exothermic reaction

while liberating the rare earth metal is made to react with the compounds of rare earths. According to the operating conditions, this is obtained in the solid or molten state, separable or non-separable from other elements of the reaction, or it gives an alloy with an excess of the reducing metal. Finally, another principle of separation has been recently used, interconnected with that of displacement; it is the principle of elimination by distillation of the rare metal displaced. It is known that L. Hackspill has made the best use of this application of Berthollet's law for preparing alkali metals (28).

We shall examine successively the displacement of rare earth metals by alkali metals, with Al, Mg, alkaline earth metals and finally, the rare earth metals themselves, particularly the action of lanthanum on compounds of other elements.

(A) **Displacements by alkali metals:**

Mosander, in 1826 (29), obtained powdered cerium by the action of potassium on $CeCl_3$. In 1842, Beringer (30) utilised Na to obtain a similar powder. We also find the names of Marignac (31), Wöhler (32) and Kremers (18) in the use of these very reactions.

Zintl and Neumayr (33) made the vapours of Na react with heated $CeCl_3$. The cerium obtained is powdery and mixed with NaCl.

In 1937 Klemm and Bommer (34) utilised the action of alkali metals, and particularly that of potassium on chlorides of rare earths, for preparing all the metals except promethium. The reaction is carried out at 250° and an intimate mixture of rare earth metals and alkali chloride is obtained. This arrangement was favourable to the authors for studying with X-rays the structures of rare earth metals, the alkali salt permitting directly a standardisation of X-spectrum. Nevertheless, it was not possible to obtain, by this process, rare metals in compact form, separated from their chloride gangue.

Finally in 1948, Asprey, Eyring and Heppler (35) tried to reduce the trifluorides of europium, samarium, gadolinium and lanthanum by sodium vapour at 1200°C in BeO crucibles. They do not seem to have obtained the metals.

(B) **Displacements by Al:**

Various attempts have been made to displace the rare earth metals by Al, either from their oxide, or from their halogenated compounds. In certain cases, alloys were obtained but it does not seem that we could dissociate them in order to obtain the rare earth metals. In particular, Schumaker and Harris (20) have been able to displace the salts of erbium and gadolinium with molten Al and obtained the alloys. The distillation of excess Al at high temperature could not be carried out; azeotropes with 10% erbium and 60% gadolinium were formed.

(C) **Displacements by Mg:**

The action of Mg, as a reducing element capable of displacing rare earth metals, has been first tried on oxides. In fact, it is interesting to try to avoid the arduous preparation of anhydrous chlorides and displace directly the rare metal from its oxide.

Winckler, in 1890 (36), Matignon, in 1900 (37), Holm, in 1902 (38) used this process. A mixture of magnesia and rare earth metal was obtained which was detected, in the case of cerium, by its pyrophoricity. Nevertheless, the metal-oxide separation has not been carried out.

It is easier to obtain alloys than pure metals by the action of excess Mg on rare oxides.

To show the possibilities of attack of oxides by Mg, F. Mahn (39) dipped in molten Mg oxide blocks which had been fused previously in a solar furnace. There is no reaction at 800° but at 1050°, a rather rapid attack of compact neodymium oxide by Mg can be obtained. The alloy assays about 5% of neodymium.

Under the same conditions, gadolinium oxide and the mixture of yttrium earth oxides give alloys of very low assay, in spite of a very high reaction time.

It is with chlorides and fluorides that more satisfactory results have been obtained.

F. Trombe and F. Mahn (40), by the action of molten Mg on fused chloride, in molybdenum crucible, obtained Mg alloys of cerium, neodymium and gadolinium. For each of these tests, an optimum temperature, which seems identical in the three cases, has been defined: it is of the order of 800°.

It may be pointed out that this reaction can give alloys of very high concentrations when molten Mg occupies the lower position with respect to the fused salt-bath. Now, normally, on account of its relatively low density, it is found above. The passage of Mg to the bottom of rare earth salt bath is done by adding to the latter a diluent of low density (alkali chloride) or by adding to Mg a heavy metal (Cd or Zn). The alloy formed mixes with Mg through gravity; it is obtained homogeneously and can assay 12% of rare earth metal.

Contrary to what is observed with oxides, the yield increases with the atomic number of the inserted rare element. It may also be pointed out that this is a case of a true equilibrium reaction. The authors were able to cause the concentration of alloy revert from 12 to 2% by adding Mg Cl_2 to the fused rare earth salt bath. The disadvantage of this method lies in the impossibility of displacing the entire rare earth metal because of the formation of $MgCl_2$ by the reaction itself.

The same authors (41) have caused a more complete displacement of rare earth salts by following the reaction electrolytically, the fused alloy occupying the bottom of the crucible forming the cathode. The yields can be considerably high and the concentration of alloy exceeds 40%.

A variation of this process has been studied by F. Mahn (39). It consists of the reaction of fused Mg at 800°C with rare earth fluorides fused with a flux containing $CaCl_2$ (10 parts) and alkali chloride (NaCl) (10 parts). A fusion flux with alkali fluorides cannot be used because the latter explode in contact with Mg.

The use of rare earth fluorides presents the advantage of giving very high alloy concentrations (of the order of 20 to 25%), except for cerium, samarium and scandium. On the other hand, it is known that it is easier to prepare the insoluble anhydrous fluorides than the rare earth chlorides.

The rare earth metals are obtained from their alloys by distillation of Mg under vacuum (40). A concentration of rare earth metal of the order of 99.5% is easily obtained and, if the reaction is carried out beyond the melting point of the rare metal, a concentration of 99.8% results.

While operating in molybdenum crucibles, the temperature cannot be raised above 1200° without some attack of this metal.

The authors have pointed out that treatment at high temperature in magnesia crucibles invariably led to Mg concentrations of the order of 0.1 to 0.2%, even if the metal submitted to fusion did not previously contain Mg; there is an equilibrium between the metal and the crucible. The previous methods can lead to inexpensive preparations of rare earths metals, especially of the metals of cerium group. Thus, cerium, neodymium, praseodymium, gadolinium and yttrium have been prepared.

The distillation of samarium-magnesium alloys have shown, on the contrary (41), that the complete separation of these two metals was difficult, if not impossible, samarium being easily carried away by the vapours of Mg.

(D) **Displacements by alkaline-earth metals:**

The displacement of rare earth metals by highly electro-positive alkaline-earth metals appears, a priori, easy.

The reduction of oxides by calcium has been attempted (16) (36) but, as with Mg, mixtures of refractory oxides and difficultly separable rare earth metals were obtained.

Moldenhauer, in 1914 (42), and Karl, in 1934 (43), used the action of Ca on fused cerium chloride. Karl, in particular, has thus prepared an industrial cerium containing 1.67% of Fe and only 0.25% Co. The operation is carried out with yields of about 85-88%.

The same reaction was used by Derge and Martin (11) who also obtained yields of the same order in the preparation of cerium. These authors did not operate at a definite temperature, but studied the rise of temperatures from the reaction threshold at about 575°C.

They also employed the action of Ca on cerium bromide and lanthanum bromide. It does not appear that there is any advantage in using bromides.

We also find in literature reference to the use of Ba to displace Sm from its bromide. A Sm-Ba alloy would be obtained from which Ba could be distilled giving pure metallic Sm (44).

The use of Ba has also been recommended by Eyring and Cunningham (45) who have prepared metallic praseodymium by passing at 1100°, under reduced pressure, Ba vapour over praseodymium fluoride.

The preparations of rare earth metals by displacement from their compounds with the aid of Ca were recently taken up on a large scale in U. S. A. Spedding and his collaborators used for the preparation of rare earths metals, new materials which were at their disposal; pure Ca, on the one hand, and on the other metallic tantalum whose insolubility (distinctly higher than those of W and Mo) in fused rare earths they had recognized. Moreover, considerable quantities of pure rare earths salts were at their disposal.

The first arrangement (Diagram 3) consisted of a steel bomb 1, lined with sintered magnesia 3 or molten dolomite. At the interior of this oxide crucible was placed, in 2, the mixture of anhydrous rare earths

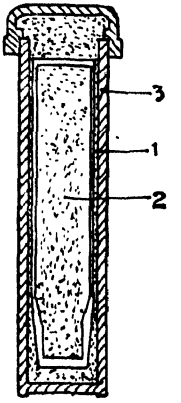

Diagram 3.

chlorides and pure Ca. The reaction was initiated by heating the bomb at 700°, but the heat liberated, for operations of small quantities was not sufficient to fuse the rare earth metals and $CaCl_2$ resulting from the reaction. Extra heat was obtained by adding 0.3 molecule of iodine per molecule of rare earths halide with, of course, excess of Ca corresponding to the formation of CaI_2 (46 to 50). The iodide also presented the advantage of giving, with $CaCl_2$, a lower melting flux. This iodide method had also been employed by Decroly (51) for the preparation of rare earth metals.

Spedding and his collaborators could prepare kilogram quantities of lanthanum, cerium, neodymium, praseodymium. The concentration of Ca in these metals was lowered to less than 150 ppm by re-fusion under vacuum in magnesia or BeO crucible.

As will be seen, this re-fusion technique was modified later on, the magnesia or beryllia crucibles being, as we have mentioned above, clearly attacked by rare earth metals.

It is by the use of tantalum that the technique of preparation could be modified in order to prepare yttrium and rare earth metals of high aomic weight. The bomb initially used was replaced by an open crucible made of tantalum and, this being heated externally at a sufficiently high temperature, the addition of iodine was given up. The reaction continued to take place at about 600°, with evolution of heat but it was possible later on, by further external heating to go up much higher in order to fuse the metal protected by the flux.

By heating to 1350°C, Spedding and his collaborators have obtained molten metallic gadolinium in considerable quantities with very high yields, close to 100%, by the displacement reaction. However, the method should still undergo some modifications in order to lead to the preparation of metals more refractory than gadolinium i.e., yttrium and metals of this group. The difficulty encountered was, in fact, the ebullition of $CaCl_2$ below the temperature of fusion of the rare earth metals. It was necessary to substitute the fluoride of rare earths by the chloride. Besides, for certain metals, like dysprosium, holmium, thulium anl lutecium, which have considerable vapour pressures at their melting point, it was necessary to maintain an atmosphere of argon under pressure over the crucible to prevent their distillation :

The use of tantalum crucibles has necessitated the perfection of a fusion technique, under helium or argon, to solder thin strips of tantalum. The tantalum crucible adheres in fact to the rare earth metal and in order to recover the latter after the operation, the surface of tantalum has to be removed mechanically. It is therefore useful, in order to avoid very great losses of tantalum, to operate with thin strips of this metal.

By the above methods, Spedding and his collaborators (46 to 50)

(52) (53) have been able to prepare all the metals of rare earths with the exception of Sm, Eu and Yb in which elements, instead of a metal, a bivalent halide results.

Daane (48) has used this phenomenon to separate gadolinium from Sm and Eu. A gadolinium chloride with 2% Sm gives, on treatment with Ca, metallic Gd without Sm, even if the ratio of these two elements in the gangue becomes equal to about 1:1. He has also observed that, in this treatment, Eu follows Sm into the gangue and is not found in Gd.

(d) Use of vapour pressures of rare earth metals for their separation and purification

For a long time it has been known that certain rare earth elements such as lanthanum are difficult to distil (1) (3), whereas others, such as europium (54) or even samarium (41), pass rather easily into the vapour state.

Various types of experiments have been carried out, (1) to separate rare earths among themselves, the material for distillation being the metals or some of their compounds, (2) to obtain directly the volatile metals from their salts by displacement with the aid of a non-volatile rare metal or another metal, or finally, (3) to purify a metal and separate it from its oxide and from different common elements.

(1) Separation of rare earth metals or their compounds by distillation

The problem of the separation of rare earths would have been resolved easily if compounds of this group had been found capable of passing into the gaseous state and of condensing as liquid. Since some difference in the physical properties of these elements or of their compounds exists, separations by exchange between two mobile phases would not probably present more difficulties than those, for example, of different hydrocarbons with very close boiling points.

Material capable of containing the compound in the liquid or gaseous form without being attacked by it also poses a problem. Finally, it is necessary that the compound eventually formed is stable and is not transformed, during distillation, into substances presenting physical properties different from those of the initial products.

The separation of rare earth chlorides by distillation has been attempted (55) (56), but these compounds always contain small quantities of troublesome oxychlorides. Moreover, the quartz material used is attacked during the operation.

More recently, the treatment of carbides in graphite crucibles has been done under atmospheric pressure. The carbides can be easily prepared by reduction of the oxides (57). The raw material consisted of elements of atomic number higher than 62, associated with an

appreciable percentage of yttrium. Heating to 2500-2600° of the lower part of a crucible, topped by a series of condensers made of carbon, did not give any distinct separation of the elements. Only, ytterbium carbide was found in the cold zones, clearly isolated from the others.

These tests have been taken up systematically by J. C. Achard (7), operating under vacuum instead of atmospheric pressure. The mixture of oxide (80%) and graphite (20%), placed in a graphite crucible topped by a metal water condenser, is heated to a temperature of 1350-1500°C under a pressure of 10^{-3} mm. Hg. A powerful pumping unit is necessary to maintain so low a pressure, because of the evolution of CO_2 given off by the reduction reaction. The distillate contains a mixture of protoxide and metal and 1 to 2% carbon. This method gives an excellent separation of elements with divalent character from their trivalent neighbours which remain in stable carbide state in the crucible. We obtain, for example, separations of Sm-Gd, Sm-Nd, Eu-Gd, Yb-Lu etc.

The interest of this method is increased by the fact that the divalent element, which can be eliminated by distillation, can play, initially, the rôle of a separating element in a primary classical separation (fractional precipitation, fractional crystallisation, ion-exchange). It is thus, in particular, that spectroscopically pure Lu can be obtained by distillation of ytterbium interposed initially between lutecium and thulium.

We shall see further that a second distillation of the condensed product can lead to metal.

Separations of metals from the mixture, called misch-metal, have been tried under vacuum in a molybdenum tube (57). The heating of the central part of the tube at 1500°-1600° has permitted an approximate gradation of the elements. The non-volatile lathanum remains in the crucible with a portion of cerium and praseodymium and in the condensed phase, in the order of decreasing temperatures, are found cerium, praseodymium, neodymium and samarium. The separations are not complete, but neodymium, and farther away, samarium are found in a large proportion in the coldest zones. Europium was not detected in this operation.

These tests have not been pursued, the molybdenum tube being seriously attacked at 1500° by the rare metals present in the liquid or vapour state. The use of tantalum has permitted Spedding and Daane (53) to realise, under the best conditions, the fractional distillation of metals. In their experiments, 80 gms of rare earth oxides, containing principally Lu, Yb, Tm, Er, Ho, Dy, Gd, Sm, were mixed with 100 gms of freshly prepared La turnings and placed in a tantalum crucible above which was arranged a fractionating column made of tantalum, containing 16 plates placed 2.5 cm apart. This assembly was heated for 30 minutes in vacuum, the crucible containing the charge

being raised to a temperature of 1600°. The temperature along the column varied from 1600° to 600°. Pure metals were not obtained but only very rich accumulations, especially of Sm and Yb. The order of volatility observed was Eu, Yb, Sm, Lu, Ho, Dy, Er, Gd La.

(2) Preparation of rare metals by displacement and distillation.

The 3 elements with divalent character Sm, Eu, Yb can be obtained as products of distillation by the action of different reducing agents on the oxides e.g., La, Ca and even C.

(a) Action of lanthanum :

Daane, Dennison and Spedding (58) have perfected the following method of preparation : La, the least volatile of all the rare earth metals, is mixed thoroughly with the oxide of the metal that is to be distilled. The mixture is placed in a welded tantalum crucible which is heated only in its lower half. Heating to 1450° for 30 minutes in a vacuum of one micron has permitted the volatilisation of Sm and its deposition on the coolest parts of the crucible. The metal is more than 98% pure and does not contain La.

Ytterbium has been prepared by the same method. It seems more volatile than Sm, for it is sufficient to heat the crucible to 1350° in order to obtain its deposit. Europium, still more volatile than the preceding metals, can be distilled under vacuum at a still lower temperature.

(b) Action of calcium

Onstott (59), taking as a basis the theoretical considerations of Glossner, succeeded in using Ca in place of La as a reducer of samarium oxide. He obtained calcium oxide and Sm which distilled over. The operation, carried out in a tantalum crucible, involves 2 stages : (1) heating to 1000°, either in vacuum, or in purified argon, during which the reduction of oxide takes place. (2) heating to 1100°, permitting the distillation of Sm and excess of Ca. After 3 or 4 distillations, the Sm obtained contained less than 0.1% calcium.

The author also observed that the fractions of relatively pure Sm had the brilliancy of freshly cut iron and were easily detachable from the tantalum plate on which they had been deposited. On the contrary, fractions rich in Ca adhered strongly on tantalum and presented a yellowish coloration different from that of pure Sm. This method seems more laborious than the La method.

(c) Action of carbon

By the process described above, J. C. Achard (7) obtained mixtures of protoxides and metals with 1 to 2% C in the first distillation. A second distillation of the condensed product is carried out in a tantalum apparatus, under a pressure of 10^{-4} and 10^{-5} mm Hg. The

following results are obtained : The second distillation of Sm, between 1300 and 1400°, can lead, in certain operating conditions, to a white brillant and malleable metal.

The x-ray diagram of this metal nevertheless gives very weak principal lines of protoxide. The same operation on Eu at 1200°C leads also to a malleable metal with protoxide bands weaker than in the case of Sm. Metallic ytterbium similarly obtained is equally malleable. According to the x-ray analysis, it is free from protoxide.

(3) **Application of distillation to the purification of rare metals**

When it is a question not of separating several rare metals but of purifying one of them in order to especially free it from its oxide or from certain common elements, the distillation operation presents features other than those which lead to a fractional separation. The crucible containing the material to be distilled, while being refractory, can have a slight solubility in fused rare metals. It is enough if it has an extremely small vapour pressure at the temperature at which the operation is carried out. The condenser can be composed of the same metal if its temperature is such that the metal to be condensed deposits in the solid form. Under these conditions, the metal distilled is not contaminated by its support.

The purification of metallic dysprosium by distillation has been done according to the preceding technique (57) (60). The apparatus includes a tungsten block intended to serve as condenser placed over a molybdenum crucible which carries at its bottom a crucible, also made of molybdenum, containing the metal to be distilled. The whole assembly is placed in a pyrex container in which a high vacuum can be maintained. Heating to high temperature is carried out by high-frequency induction with the aid of a winding which can be displaced in height along the pyrex cylinder. Each operation involves quantities of the order of 1 gm.

To obtain a compact deposit of dysprosium, the tungsten block is preheated upto a temperature of the order of 800°, then the lower crucible is heated in its turn, by modifying the position of primary winding, to 1400-1500° for about 10 minutes. Dysprosium is deposited on the surface of the condensing crucible from which it is detached by simple hammering. This compact dysprosium seems to be free from impurities. In the molybdenum cup, a black oxide residue containing silicon and a small quantity of iron is found. It is probable that this method of purification of rare metals will become generalised.

Purity of metals obtained : influence of certain elements on their physical properties.

In the early stages the rare earth metals were most often prepared from partially purified raw materials and the elements were not

properly separated from one another. During the last 25 years the use of rather pure rare earths has resulted in the preparation of metals containing less than 0.5% of other elements of their group.

We know, especially from the magnetic properties, certain aspects of the influence of rare earth impurities on the behaviour of oxides (61). But the influence of rare earth metals on one another, when it concerns their physical properties, is not very defined. It will certainly be very interesting to study, from different points of view, the diagrams which the rare earth metals give among themselves. The role played by certain elements of other groups on the physical properties of a few metals of rare earths is well known.

The different methods of preparation can bring in the following impurities : direct electrolyses, carried out in C crucible, give a few % of carbon, according to the operating conditions; similar concentrations of silicon are obtained by the use of silica crucibles; porcelain crucibles with fluorspar give very small amounts of impurities, generally silicon and iron ; the electrodes made of tungsten, and particularly molybdenum, are not at all corroded below 1000°; tatalum seems still less attacked by rare earth metals.

The operations involving the intermediate formation of alloys (Cd or Zn) can lead to very pure metals if the material for electrolysis is itself well purified. It has been found, by spectrographic control (1), that Cd can be totally separated from rare earth metals by distillation.

The displacements by magnesium lead to metals containing 0.1% Mg and some of the impurities of the latter metal. It is possible that we can eliminate Mg totally from rare earth metals by the use of a tantalum crucible for the treatment under vacuum. In fact, as has already been said, the treatment in magnesite crucible always gives 0.1% Mg in the rare earth metal, even if the latter did not contain some of it before fusion.

The displacements by Ca give metals which, after fusion under vacuum, could contain less than 150 ppm of Ca (46 to 50), (52), (53). Spedding and his collaborators have prepared, by this method, rare earth metals from salts specially purified with the aid of ion exchange. We think that the rare earth impurity has always been lower than 1% in Spedding's experiments. The Ca impurity resulting from the metallurgical treatment can be reduced, as has been said, to 150 p.p.m. by as rapid a refusion as possible in tantalum crucible, but we introduce in this operation tantalum impurity, of the order of 1000 p.p.m. for tests on small scale or even 500 p.p.m. for preparations with considerable quantities. It is necessary to point out here that the tantalum content can exceed by far the above values. The assaying of tantalum is sometimes difficult by arc spectrography, tantalum carbide being very refractory. A better detection is obtained through radioactivation technique.

Spedding also points out that a satisfactory method for the analysis of oxygen in rare earth metals has not yet been found. Nevertheless, he has carried out a metallographic examination which indicates that there could remain about 0.1 to 0.5% oxygen in metals, which would lead to significant oxide concentrations. It is logical to think, as has been stated by Daane (48), that there remains less oxygen in metals remelted in tantalum crucibles than in those which have been remelted in oxide crucibles, particularly in magnesite crucibles.

Spedding also indicates that, by distillation under high vacuum, metals containing much less oxygen are prepared. This technique has been used for certain elements of the group like Sm, Eu, Dy and Yb. It is more difficult to use it for La but, as earlier mentioned (4, 5), it is possible. Thus, for rare earth metals, as for many metals of other groups, distillation is the only technique of advanced purification, by which we can get rid of compounds which may originate from the metal to be purified as well as different impurities resulting from the metallurgical technique and corrosion of the distillation crucible. It may be emphasized once again that the pure metal can be condensed on a metallic wall maintained at a temperature at which it is not attacked. The crucible used for the distillation, as we have mentioned it in the case of tungsten (57), may itself be slightly attacked, but that is not of importance if the dissolved material does not pass into the vapour phase.

The role of impurities on the physical properties of the rare earth metals seems to be very irregular. The influence of iron on the magnetic properties of cerium has been studied systematically by Ch. Henry Blanchetais (61) (62). It is necessary to decrease the concentration of Fe in Ce to 5 ppm in order to obtain the correct magnetic behaviour of the latter. Nevertheless, a few ten-thousandths of iron do not modify the position of magnetic anomalies of Ce, but only the general shape of the susceptibility curve as a function of temperature. In other rare earth metals, it does not seem that traces of Fe modify considerably the observed magnetic properties; iron, initially in the form of alloys, seem to be precipitated in the free state (63) when Mg concentration exceeds 60%.

Carbon gives a carbide of the type MC_2 with rare earth metals. Besides, the carbide can, under certain conditions, remain as solid solution in the metal. The magnetic properties and the coefficient of dilatation seem uninfluenced by small traces of carbon. On the other hand, the mechanical properties can be considerably modified.

Silicon, in small proportions (say a few thousandths), also seems to influence the mechanical properties, but has very little influence on the magnetic properties and on different transformations which the rare earth metals undergo. A systematic study of cerium containing 0.4%, 0.07% or 0.05% of Si has not shown any modification of the dilatometric transformation at low temperature $\beta \leftrightharpoons \beta c$ (64). Si and Fe do not seem to enter, except in very small proportions, as solid solution

in Ce. This conclusion agrees with the fact that the atomic volumes of Fe (7.1) and Si (12.04) are considerably different from that of Ce (20.8). In comparison Mg (atomic volume 14) and Ca (At. vol. 26) behave quite differently from the preceding metals.

Systematic studies of the influence of Mg on Ce and Gd have been made by F. Mahne (65 to 69), which show, as we shall further see in detail, that the dilatation anomaly at low temperature, which is maximum for pure metal, decreases regularly with increase of Mg concentration and only disappears when the alloy contains 1% Mg. The magnetic anomaly also disappears for the same concentration, but presents an amplitude much greater than that which could be observed for the pure metal when Ce contains 0.21% Mg.

Gadolinium which, in the pure state, is ferromagnetic and presents a Curie point at 289°K has its magnetic properties completely modified by an addition of 2% Mg, when another Curie point is observed at 266°K. It appears therefore that Mg, in low concentration, has a very important influence on the behaviour of rare earth metals.

The influence of Ca has not been very much studied but allotropic transformations of Ce are suppressed by a small concentration of Ca, of the order of 1%.

The two metals, Mg and Ca, should therefore be particularly eliminated from rare earth metals if we want to have definite results, especially for magnetic measurements.

We know little about the solubility, at different temperatures, of W, Mo and Ta in the rare earth metals, diagrams being apparently not established. The influence of these elements on the physical properties of the rare earth metals is not known. It is probable that it is small, if the separation in the solid phase, on cooling, is carried out totally, as this seems to be the case for Mo in metals with low melting points such as cerium.

An Outline of the Physical and Chemical Properties of Rare Earth Metals

It seems indispensable, following the description of the preparation of rare earth metals, to give an idea of their physical and chemical properties. In order not to extend too much the previous statement, we shall give only a very schematic outline of these properties, while stressing on a few exceptional characteristics of the rare earth metals, e.g., super-conductivity of La, anomalies of Ce, ferro- and antiferro-magnetic properties, action of pressure on the behaviour of rare earth metals.

The names of authors are not mentioned in the text but are recalled in the complete bibliography.

(A) **Physical Properties**

The rare earth metals present a metallic lustre which, in the absence of any oxidation, would be intermediary between that of iron and silver. This lustre disappears very rapidly for the first elements of the group and for Eu; on the contrary, Sm, for example, can be kept in air for several months.

—Crystalline Structure : (Complete Bibliography No. 70 to 104).

La, Ce and Pr are known in two crystalline structures: α , compact hexagonal and β, cubic face-centered. Sm is rhombhohedral but the piling of atoms in the successive layers is such that its structure is apparently narrowed at the same time to the compact hexagonal structure and to the cubic face-centred structure. Europium, very probably a bivalent metal, has a different structure in the series of lanthanides : it is cubic-centered and its density is abnormally low. Yb, an equally bivalent metal, is cubic centred, but its density is also very small, in accordance with its position in the rare earth group. Other metals of yttrium group, like yttrium and scandium are known only in the compact hexagonal form (see table I).

The measured densities are rather similar to those which are calculated from the structures (see table II).

TABLE—II

Element	La	Ce	Pr	Nd	Sm	Gd	Dy	Ho	Er	Tm	Yb	Lu
Measured density (Bridgman)	6.15	6.9	6.5	6.91	7.50	7.96	8.45	8.76	9.04	9.26	7.02	9.81

—Mechanical properties : (Complete Bibliography : N. 127-141).

On the whole, the rare earth metals are soft (20-30 Brinell units), but the hardness seems to increase with the atomic number, at least up to gadolinium. They are malleable when they are pure. The malleability of Yb may be specially mentioned.

—Dilatations : (Complete Bibliography : No. 142 to 156).

In the cases where they do not present any transformations, the rare earth metals have normal expansion co-efficients, which appear to increase slightly with the atomic number. The co-efficients, at the ordinary temperature, are of the order of 6.10^{-6} for La, 8.10^{-6} for Ce, $7.5\text{-}10^{-6}$ for Nd, and 8 to $10\text{x}10^{-6}$ for Gd and Dy, $10\text{x}10^{-6}$ for Er.

TABLE—I

Element	Purity %	Structure	o a (A)	o C (A)	Atomic radius	Atomic Volume (cm^3)	Calculated density	Authors
Sc	99.6	Hexag. comp.	3.3090	5.2733	—	—	—	Spedding, Daane, Herrmann
Y	—	Hexag. comp.	3.663	5.814	1.814	20.46	4.34	Quill
Y	99.4	Hexag. comp.	3.6474	5.7306	—	—	—	Spedding, Daane, Herrmann
α La	—	Hexag. comp.	3.754	6.063	1.870	22.43	6.194	Quill, Klemm, Bommer
α La	99.8	Hexag. comp.	3.770	12.159	—	—	—	Spedding, Daane, Herrmann
βLa	—	Cube faces cent	5.294	—	1.872	22.48	6.180	Klemm, Bommer
α Ce	—	Hexag. comp.	3.65	5.96	1.81	20.7	6.78	Hull
βCe	—	Cube faces cent	5.140	—	1.817	20.58	6.810	Quill, Klemm, Bommer, Audrieth
βCe	99.9	Cube faces cent	5.1612	—	—	—	—	Spedding, Daane, Herrmann
α Pr	—	Hexag. comp.	3.657	5.924	1.824	20.79	6.777	Rossi
α Pr	99.9	Hexag. comp.	3.6725	11.8354	—	—	—	Spedding, Daane, Herrmann
βPr	—	Cube faces cent	5.151	—	1.821	20.71	6.805	Rossi, Klemm, Bommer
Nd	—	Hexag. comp.	3.655	5.880	—	20.62	6.998	Quill, Klemm, Bommer, Audrieth
Nd	99.8	Hexag. comp.	3.6579	11.7992	1.819	—	—	Spedding, Daane, Herrmann
Sm	99	Rhomb.-Hex: comp.	3.621	26.25	—	—	—	Daane et collab.
Eu	—	Cube centre	4.573	—	2.042	29.00	5.244	Klemm, Bommer
Eu	98-99	Cube centre	4.606	—	—	—	—	Spedding, Daane, Herrmann
Gd	—	Hexag. comp.	3.622	5.748	1.794	19.79	7.948	Klemm, Bommer
Gd	99.7	Hexag. comp.	3.6360	5.7826	—	—	—	Spedding, Daane, Herrmann
Tb	—	Hexag. comp.	3.585	5.664	1.773	19.11	8.332	Klemm, Bommer
Tb	99.9	Hexag. comp.	3.6010	5.6936	—	—	—	Spedding, Daane, Herrmann
Dy	—	Hexag. comp.	3.578	5.648	1.769	18.97	8.562	Klemm, Bommer
Dy	99.8	Hexag. comp.	3.5903	5.6475	—	—	—	Spedding, Daane, Herrmann
Ho	99.4	Hexag. comp.	3.5773	5.6158	—	—	—	Spedding, Daane, Herrmann
Er	—	Hexag. comp.	3.532	5,589	1.748	18.29	9.164	Klemm, Bommer
Er	99.8	Hexag. comp.	3.5588	5.5874	—	—	—	Spedding, Daane, Herrmann
Tm	—	Hexag. comp.	3.523	5,564	1.742	18.12	9,346	Klemm, Bommer
Tm	99.9	Hexag. comp.	3.5375	5.5546	—	—	—	Spedding, Daane, Herrmann
Yb	—	Cube faces cent	5.468	—	1.933	24.76	7.010	Klemm, Bommer
Yb	99.9	Cube faces cent	5.4862	—	—	—	—	Spedding, Daane, Herrmann
Lu	—	Hexag. comp.	3.509	5.559	1.737	17.96	9.740	Klemm, Bommer
Lu	99.9	Hexag. comp.	3.5031	5.5509	—	—	—	Spedding, Daane, Herrmann

—Specific heats: (Complete Bibliography: No. 157 to 170).

At ordinary temperature, the specific heat of rare earth metals is of the order of 0.03-0.05, corresponding to an atomic heat close to 6 cal./at. gr.-degree. The specific heat curve as a function of temperature permits to detect, in a very sensitive manner, the different anomalies (supraconductivity, change of allotropic state, Curie point, Neel point) which most of the rare earth metals exhibit.

Melting points (Complete Bibliography No. 171-188)

The rare earth metals are, on the whole, relatively refractory, principally those of the yttrium group (see table 3-4). For the metals of Ce group, such as Yb, which melt at temperatures lower than 1000°, the melting points have been determined by thermal analysis, the temperature being measured by means of a thermo-couple.

TABLE—III

Melting points of a few rare earth metals

Element	M.P.	Authors
La	885° C	Trombe
	920°	Spedding et Daane
Ce	815°	Trombe
	804°	Ganneri et Rossi
Pr	932°	Spedding et Daane
	935°	Spedding et Daane
Nd	1024°	Spedding et Daane
Sm	1052°	Spedding et Daane
Yb	824°	Spedding et Daane

TABLE—IV

The estimated melting points of a few rare earth metals

Element	Estimated M. P.	Authors
Eu	1100° — 1200° C	Trombe
Gd	> 1200°	Trombe
	1350°	Spedding and Daane
Tb	1400 to 1500°	Spedding and Daane
Dy	1400 — 1500°	Trombe
	1500°	Spedding and Daane
Ho	1500°	Spedding and Daane
Er	1500 to 1550°	Spedding and Daane
Tm	1550 to 1650°	Spedding and Daane
Lu	1650 to 1750°	Spedding and Daane
Sc	1400°	Fisher, Brunger et Grieneisen
Y	1500°	Spedding and Daane

For the metals of yttrium group are available only estimates of the melting points obtained by adjusting, by means of an optical

pyrometer, the temperature at which the metals are cast (Spedding and Danne).

Vapour pressures and boiling points (Complete Bibliography No. 189-200)

Table V (according to Spedding and Daane and Ahmann) gives the vapour pressures at different temperatures of a few rare earth metals. The temperatures of ebullition, determined by extrapolation from the previous data, are also indicated.

TABLE—V

Vapour pressures of a few rare earth metals at different temperatures (°K).

P(mmHg)	La	Ce	Pr	Nd	Dy
1	2,604 °K	2,021 °K	2,123 °K	2,040 °K	1,736 °K
10^{-1}	2,271	1,860	1,889	1,805	1,552
10^{-2}	2,013	1,723	1,702	1,620	1,404
10^{-3}	1,808	1,604	1,548	1,466	1,278
10^{-4}	1,641	1,501	1,420	1,177	1,340
760	4,515	2,690	3,290	3,164	2,564

Separation test, by distillation under high vacuum of Sm, Yb and Eu, indicate that these metals possess vapour pressures higher than 10^{-3} mm Hg for the respective temperatures of 1450°, 1350° and 1000°.

Thermal effects: (Complete Bibliography : No. 201 to 207)

Thermal analysis of the metals of the cerium group as well as of Yb has brought into evidence a second isothermal stage at temperatures lower than those of their melting points, (table VI). This phenomenon is emphasized by a certain number of other anomalies (especially anomalies of resistivity), but its mechanism has not yet been elucidated.

TABLE—VI

(According to Spedding & Daane)

Element	M.P.	Second Isothermal stage
La	920° C	868°C
Ce	804	754
Pr	935	798
Nd	1024	868
Sm	1052	917
Yb	824	798

Electrical Properties

(a) **Resistivity:** (Complete Bibliography: No. 208-226)

The study of the variation of resistivity as a function of temperature of different rare earth metals shows numerous anomalies corresponding

to the exceptional properties of these metals (supraconductivity, allotropic transformations, ferro- or antiferro-magnetism).

The study of resistivity under pressure also reveals extremely interesting phenomena. Table VII gives, according to Bridgman, the values of resistivity, at 0°C and under normal pressure, for the rare earth metals.

TABLE—VII

Element	La	Ce	Pr	Nd	Sm	Gd	Dy	Ho	Er	Tm	Yb	Lu
P x 10^6	62.4	76.7	73.7	71.8	88	140.5 134.5	56	87	107	79	30	79

(b) **Supraconductivity :** (Complete Bibliography : No. 227-233).

Various authors have indicated for lanthanum, a change of supraconductivity at temperatures between 4.2 and 5.8°K. The dispersion of results is important and the disagreement remains still unexplained. The anomaly of specific heat, which supports the phenomenon of supraconductivity, is situated at 4.37°K (figure (1)).

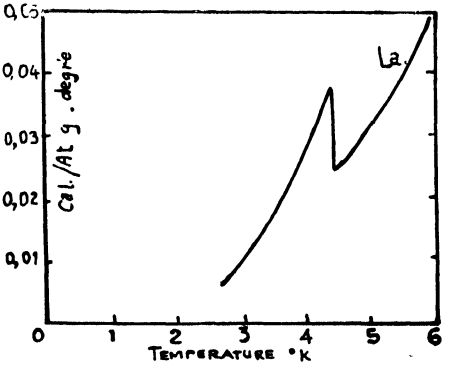

Figure 1

—**Magnetic Properties :** (Complete Bibliography : No. 234-269).

A certain number of rare earth metals possessing an empty or saturated inner orbit and which should be diamagnetic, exhibit in fact, a very low paramagnetism independent of temperature. These are Sc, Y, La and very probably Lu.

All the other rare earth metals are paramagnetic in a certain range of temperature. Besides, in a more restricted interval within this range, almost all of them follow *Curie–Weiss Law* $\chi\ (T-\theta)=C$. The paramagnetic moment deduced from this law is generally that of the

corresponding trivalent ion. An exception should be made for Eu, and probably for Yb, which for the most part are bivalent ions, as well as for Sm whose behaviour is abnormal and which does not follow Curie-Weiss Law.

Moreover, different metals like Gd, Dy, Er and probably Ho and Tb present quite exceptional magnetic properties, ferro-magnetism and antiferro-magnetism.

—Hall Effect: (270).

Y, La, Ce, Pr and Nd have been studied from 20.3° to 300°K; Gd, Dy, Er, above their respective Curie points, but no variation assigned either to the sign or to the order of magnitude of Hall coefficient has been observed in the rare earth group. Y, La, Gd and Er show negative Hall effects at all the temperatures studied; Ce, Pr, and Nd, positive Hall effects. For Dy, the Hall coefficient is positive up to 130° K and negative from 130 to 300° K. The values obtained at room temperature are the following (table 8) :

TABLE—VIII

Hall coefficient of a few rare earth metals at room temperature

Element	Y	La	Ce	Pr
Hall coefficient (V-cm|A-Oe)	$-0.770.10^{-12}$	$-0.8.10^{-12}$	$+1.81.10^{-12}$	$+0.709.10^{-12}$
Element	Nd	Gd*	Dy*	Er*
Hall coefficient (V-cm|A-Oe)	$+0.971.10^{-12}$	$-0.95.10^{-12}$	$-1.3.10^{-12}$	$-0.341.10^{-12}$

* Values calculated from "ordinary" Hall coefficient.

—Allotropic transformations of metallic cerium: (Complete Bibliography : No. 278-301).

β-Cerium (cubic face-centered) presents, at low temperature, a very important transformation which is manifested by anomalies, between 100° and 170° K, for all the physical properties of the metal.

The anomalies, at decreasing temperature, are situated at about 100°K, at increasing temperature, at about 170°K. Especially at low temperatures, we observe a contraction of 16% in volume in the crystal lattice without any change of structure (transformation $\beta \rightarrow \beta c$). This increase of density, obtained on a compact crystalline structure, has led to the hypothesis of the migration of an electron from the 4f layer to the 5d layer. The above contraction can also be obtained at the ordinary temperature by applying a pressure of 15,000 kg|cm² on cerium.

The transformation $\beta \rightarrow \beta c$ is accompanied by an increase of electri-

cal conductivity and by a considerable diminution of magnetic susceptibility. The Hall coefficient also undergoes a cycle of thermal hysteresis similar to that of electrical resistivity.

The β form (face centered cubic) is obtained by the relatively rapid cooling of pure Ce, particularly from 600° to 400° K. If in the same temperature range, the cooling is very slow, we can by repeated cycling between the temperature of liquid nitrogen and the ordinary temperature, obtain a practically complete transformation from cubic face centered cerium into compact hexagonal-cerium of ∝ -form. The curve in figure (2) represents schematically these phenomena.

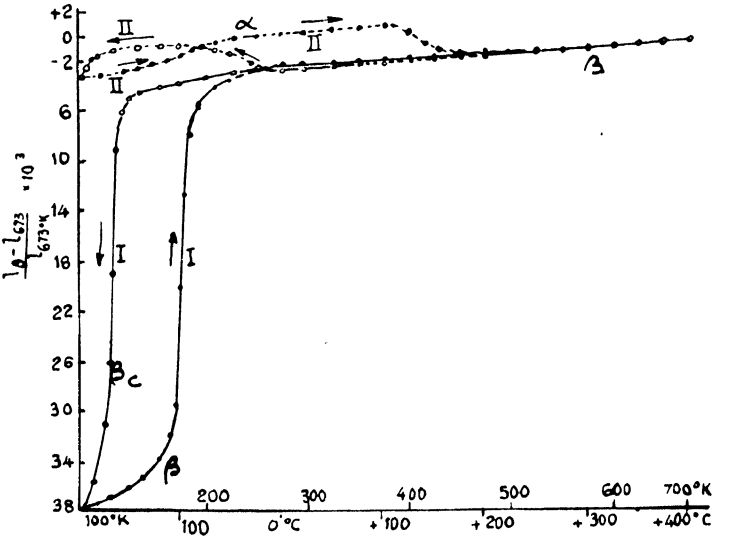

Figure 2

Once again, we can obtain the β-state by heating ∝ Ce to 300° C (a heating which is accompanied by a slight contraction of the metal above 100°C) and then by rapidly cooling it up to the ordinary temperature.

The stability of β-form depends very much on the concentration and nature of the impurities which are contained in Ce. Very small concentrations of Ca and Mg (a few percent) are sufficient to render the β-state unstable. Especially in commercial Ce, it is the ∝ -state which is found. This explains why the large anomalies exhibited by pure Ce had not been detected by the study of commercial cerium.

—Ferro-and antiferro-magnetism in the rare earth group:
(Complete Bibliography: See magnetic properties)

Probably, it is from Eu onwards that saturation phenomena or even real ferromagnetism have been observed below the paramagnetic range.

Europium presents, below 104° K, saturation phenomena which become very important at the temperature of liquid nitrogen. According to a preliminary study, the ferromagnetic Curie point of this metal would be of the order of 90°K. Gadolinium has all the characteristics of a ferromagnetic element. It possesses a well characterised ferromagnetic Curie point situated at 16° C (289° K). In the ferromagnetic region, the approximate laws about saturation are of the form :

$$H.T = \sigma \propto ,T \left(1 - \frac{a}{Hi}\right)$$

and $\sigma\, H,T = \sigma\, H,O\,(1 - A\,T^2)$ or $\sigma\, H,T = \sigma\, H,O(1 - bT^{3/2})$,

In any case, the moment with absolute saturation is equal to 7. 12μB, in good agreement with the theoretical value (7.02μB) calculated on the basis that Gd is in the fundamental spectroscopic state $^8S\,^7/_2$. The moment is higher than that of iron.

The transition at Curie point is accompanied by different anomalies : the specific heat anomaly (figure 3) of the classical type, change of slope

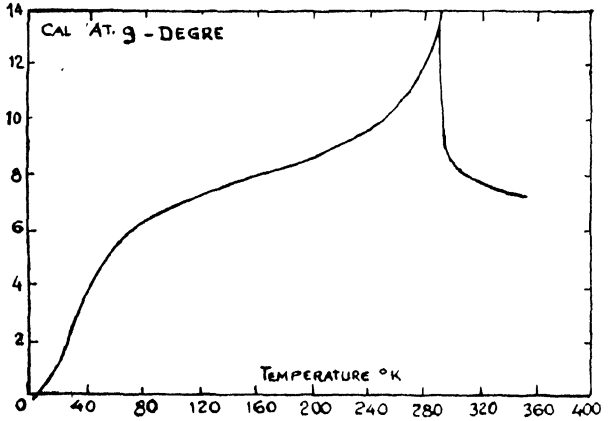

Figure 3

of the resistivity curve as a function of temperature, anomaly in the curve of Hall coefficient and the dilatation anomaly. The latter (figure 4) has a special character : the curve of dilatations $\frac{\Delta l}{lo}$, instead of presenting simply an inflection point, as for the classical ferromagnetism of the iron group, is characterised by an important horizontal stage, situated over an interval of about 150° below the curie point, and corresponding to a practically zero dilatation coefficient. The x-ray study, at low temperature, of the parameters of the Gd lattice throws light on the above result : the parameter a_0

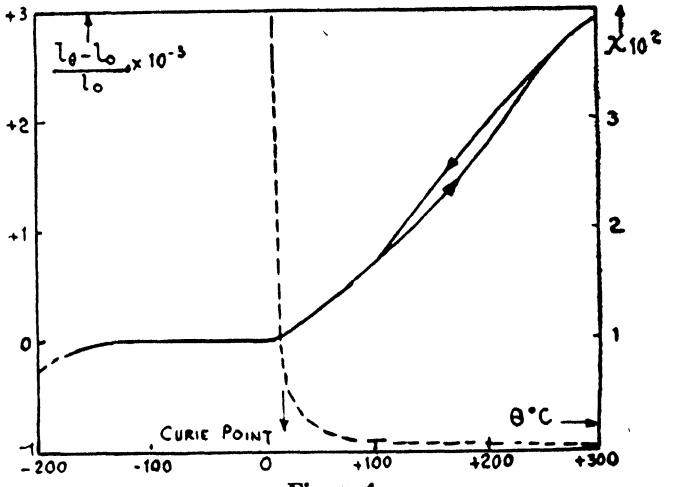

Figure 4

varies normally with temperature, while the parameter c_0 increases, in this interval when the temperature decreases.

Dysprosium has a still more remarkable magnetic behaviour (figure 5). Below the paramagnetic region, we observe a region of antiferro-magnetism between 250° K and 160° K, characterised by

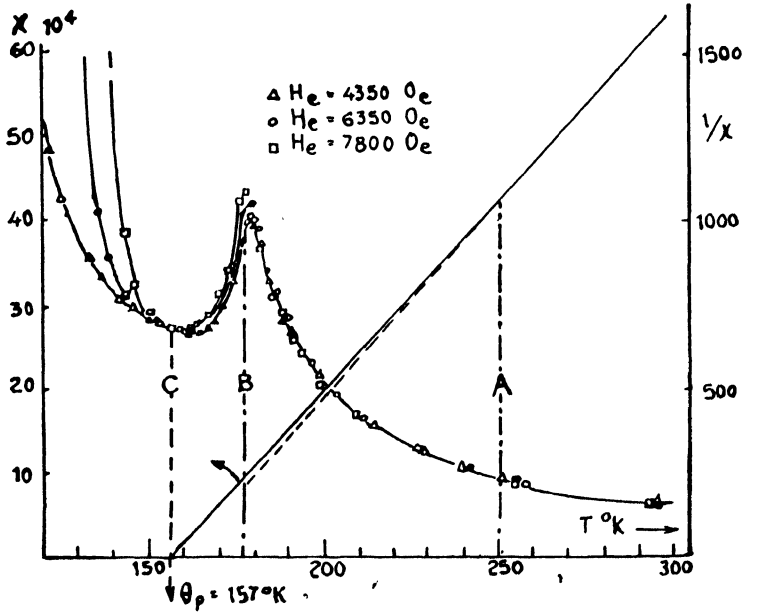

Figure 5

sharp maxima in the magnetic susceptibility at 178° K (Neel point) and a field sensitivity in the inverse direction to that which is observed for the ferro-magnetics. Below 160° K, the value of susceptibility increases rapidly and at the temperature of liquid nitrogen, the phenomena of residual magnetism and saturation characteristic of ferromagnetic behaviour are observed. The ferromagnetic Curie point θ_f is at about 85°K.

The determination of the absolute saturation moment of Dy presents an uncertainty on account of the abnormal behaviour of this metal below 31° K. In any case, the magnetic moment, 8.7 or 8.0 μB, is still higher than that of Gd.

Physical phenomena accompanying the peculiar magnetic points of Dy, Curie point and Neel point are quite analogous to those which are observed at the Curie point of Gd : the anomalies of specific heat (figure 6) involving two maxima, one at the Neel point, and the other

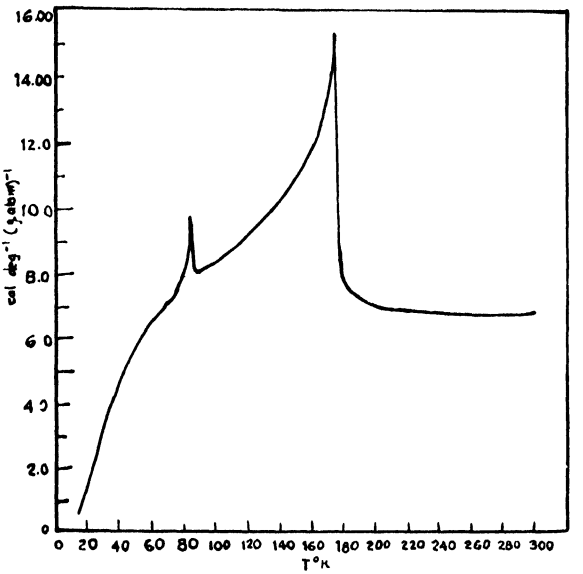

Figure 6

weaker one, at the Curie point, anomaly of electrical resistance and of Hall coefficient, and the dilatation anomalies (figure 7) corresponding to practically zero values of the dilatation co-efficient below the Neel temperature and probably below the Curie temperature.

Holmium shows at 130° K an important anomaly of the specific heat curve which predicts an exceptional magnetic behaviour of this metal at low temperature.

Erbium presents a great similarity with dysprosium. A susceptibility anomaly comparable with the Neel point of Dy, but much more pronounced is observed at 80°K. For temperatures lower than 60°K, the

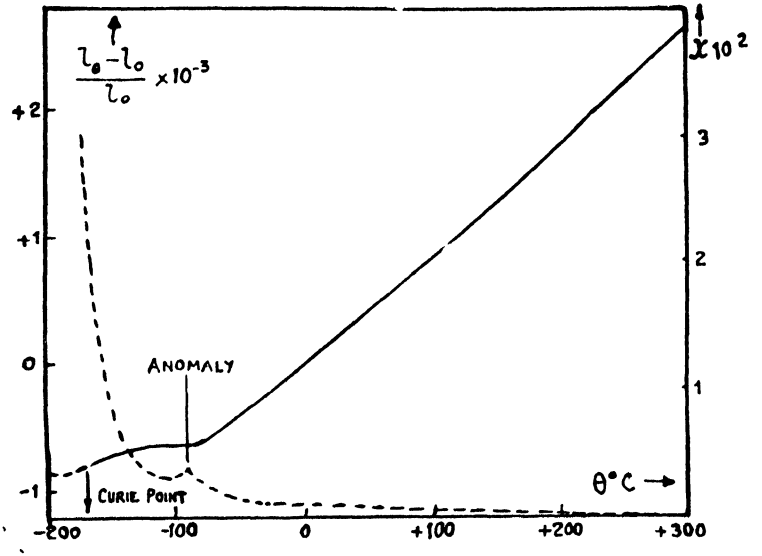

Figure 7

susceptibility is highly dependent on the applied field. The ferro-magnetic Curie point of Er would be in the vicinity of 20.4° K.

The electrical resistance curve also presents a change of slope at 80° K and a study with x-rays shows that the dilatation co-efficient of the metal, of the order of 10.10^{-6} above 100°K, would practically be zero below this temperature.

Finally, terbium would present a Curie point in the vicinity of 233° K.

—Influence of pressure on some physical properties of rare metals (Complete Bibliography : No. 271 to 276).

(a) *Variations of volume under pressure.*

The compressions $\Delta V/V_0$ have been studied up to pressures of 100,000 kg|cm^2 for a certain number of rare earth metals. Considerable diminution of volume of Ce which takes place between 10,000 and 15,000 kg|cm^2 (figure 8), corresponding to the transformation $\beta \rightarrow \beta c$, has already been pointed out. In the case of Yb also a large diminution of volume is observed, but this takes place progressively. La and Gd also show anomalies, but these are of small importance.

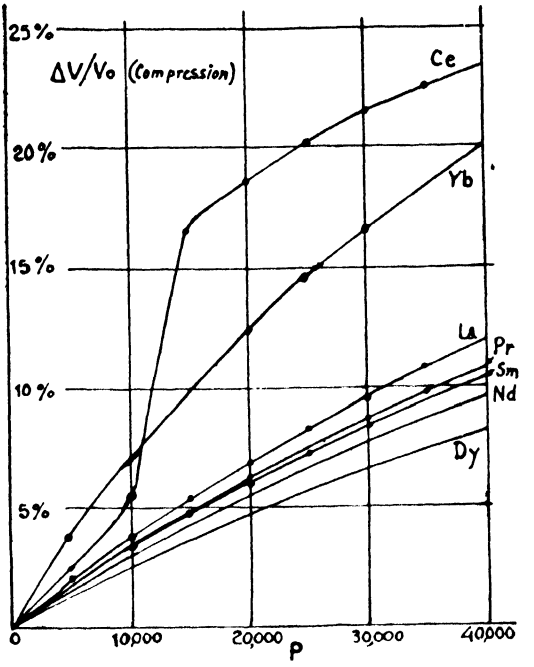

Figure 8

(b) *Influence of pressure on resistivity.*

The variations of resistivity of rare earth metals as a function of applied pressure are also of very great interest (figure 9). In particular, the vertical fall of resistivity of Ce at the moment of its change in volume is significant. Gd also shows a non-reversible, important

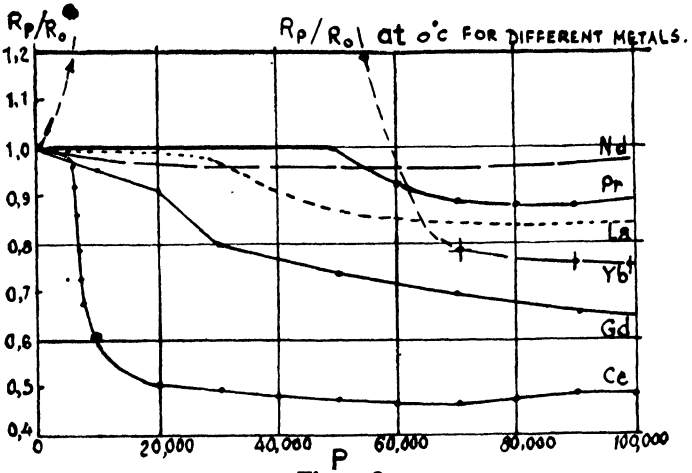

Figure 9

diminution of resistivity. La and Pr too show a special behaviour but the most remarkable phenomenon is the extraordinary increase of the resistivity of Yb. Under 50,000 Kg pressure, ytterbium has a resistance nearly 13 times greater than that under normal pressure and 16 times greater than that under 100,000 kg/cm^2 (figure 10). Measure-

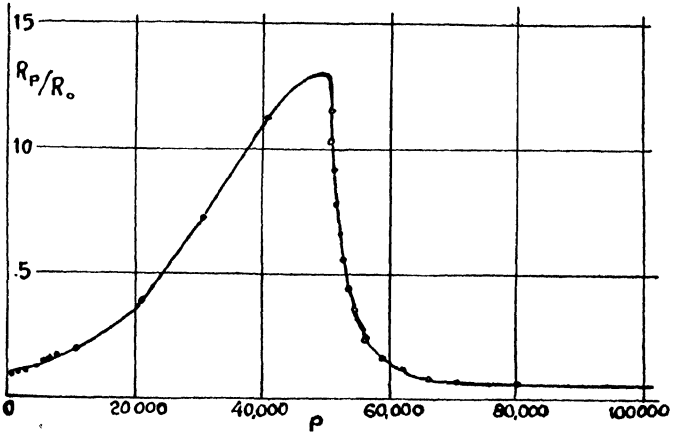

Figure 10

ments carried out on Yb, between 0 and 200° under pressures upto 7,000 Kg/cm^2 also show an inversion of the temperature co-efficient of resistivity between 0 and 100°.

—Artificial radioactivity of Tm (277)

Radioactive Tm presents remarkable γ-emitting properties which permit it to be utilised as a simple, cheap and transportable x-ray unit. Its half-life is 129 days and its irradiations have a penetrating power comparable with those of an x-ray tube of 100 kv.

(B) CHEMICAL PROPERTIES.

It is known that the rare earth metals have very great reactivity, both with respect to metalloids and metals. These are also very powerful reducing agents. However, the systematic studies on the chemical behaviour of lanthanides and the kinetics of the reactions are still few in number and only the system Ln-H, Ln-N and Ln-O seem to have been studied till now with some precision.

—Action on hydrogen (Complete Bibliography : No. 302-317).

The rare earth metals react at relatively low temperatures with hydrogen. The systems Ln-H_2 (with Ln = La, Ce, Pr, Nd) have characteristics similar to those of alloys. At first, a solid solution of hydrogen in the considered lanthanide is observed, then a mixture of two phases composed of Ln and a cubic hydride of fluoride type of

formula LnH_2 and, finally, in the interval LnH_2-LnH_3, an interstitial solid solution of hydrogen in the phase LnH_2. The composition of this single homogeneous phase is a function of pressure and temperature.

With Gd, the conclusions are slightly different; from Gd to $GdH_{1.8}$, we observe, at first, a single phase composed of a solid solution of hydrogen in the metal, then a mixture of two phases : metallic Gd and a cubic hydride of fluoride type, of composition similar to GdH_2. The interval $GdH_{1.8}$- GdH_2, composed of a single phase, can be explained by a network GdH_2 lacking in hydrogen, rather than by a solubility of Gd in GdH_2. Finally, from GdH_2 to GdH_3, we observe, in a certain interval of compositions, a mixture of ideal cubic phase GdH_2 and a hexagonal phase of ideal composition GdH_3.

—Action on deuterium : (Complete Bibliography : No. 312, 318, 319).

The action of La, Ce and Gd on deuterium seems to take place following a process similar to that observed for the reaction of these metals on hydrogen.

—Action on Nitrogen : (Complete Bibliography : No. 320 to 325).

The rare earth metals react directly with nitrogen to form nitrides of the type LnN. Thus, we know LaN, CeN, PrN, NdN, SmN, EuN and YbN.

By grouping on the same graph the parameters of the lattice of the above nitrides, as a function of the trivalent ionic radii, we obtain a regular curve which consequently seems to indicate that, in their nitrides, Sm, Eu and Yb are in the trivalent state.

—Action on oxygen : (Complete Bibliography : No. 324 and 326 to 344).

The rare earth metals present a great affinity for oxygen and their oxidation is accompanied with large evolution of heat. Only a few metals, especially uranium and zirconium furnish higher heat of oxidation.

All the lanthanides can be combined with oxygen to give a sesquioxide of the type Ln_2O_3. Nevertheless, some of them can fix a supplement of oxygen, either under the fixed form, like Ce whose dioxide CeO_2 is very stable or under a more or less labile form like Pr and Tb which give respectively Pr_6O_{11} and even PrO_2, and Tb_4O_7. Finally, very recent investigations have mentioned the formation of protoxides for Sm, Eu and Yb.

A very important problem has been elucidated a few years ago. This is the mechanism of the pyrophoricity of Ce. In fact, it was known long ago that, although the heat of formation of the oxide CeO_2 was very close to that of La_2O_3, while Ce is pyrophoric, the metals

close to rare earths are not so. Moreover, the molecular volume of the final product CeO_2 is such that this oxide should be the protecting agent. The oxidation reaction would therefore be superficial and would be arrested very rapidly.

The study of oxidation of Ce has been carried out by differential thermal analysis, a continuous gravimetric study with thermobalance and a study of the oxidation products formed by x-ray diffraction or electron diffraction.

As a result of all these investigations, the dioxide CeO_2 is not formed directly on the metal but is due to the oxidation of an intermediary sesquioxide Ce_2O_3 whose structure is such that it permits rapid and profound oxidation of Ce. It is not the hexagonal sesquioxide which has already been isolated, but a cubic sesquioxide whose lacunar structure had never been shown before, and whose density, distinctly smaller than that of CeO_2, permits the penetration of oxygen deeply across the fissured layer of dioxide.

—Action on other metalloids and compounds : (Complete Bibliography : 334 and 345 to 360).

The rare earth metals react generally, in an exothermal manner, with a large number of metalloids. Let us cite the action with B, C, Si, P, As, Sb, Bi, S, Te, the halogens.

Moreover, these metals are powerful reducing agents and decompose water, CO, CO_2, CCl_4, most of the common oxides and even, (when they are in the molten state,) the refractory oxides.

They are easily attacked by dilute acids.

—Action on metals

The lanthanides react with the other metals to give rise to numerous well-defined and eutectic compounds. On the contrary, we observe very few solid solutions in the vicinity of rare metal.

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Physical properties of rare earth Metals.

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Discussions

Mr. P. P. Bhatnagar : If I understood correctly from Prof. Trombe's talk, the reduction of the rare earth salts is carried out in the liquid state and a considerable excess of alloyed Mg is left unreacted. The product is further distilled and purified. I believe that the vapour phase reduction of rare earth salts by Mg may evidently give a purer product and a more controlled reduction may be possible. It may also be possible to make the process continuous.

Dr. H. N. Sinha : In general, reactions are done in liquid phase so as to provide a fluxing medium.

Mr. P. P. Bhatnagar : Reaction can be carried out and the products collected in an entirely closed system where an inert atmosphere can be maintained, as is done in titanium production.

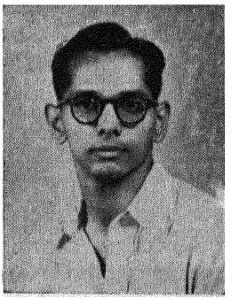
Author's reply : Vapour phase reaction has not been studied so far and may turn out to be feasible. In comparing the calcium and magnesium methods we should remember that it is difficult to prepare an alloy of magnesium and rare earths with more than 25% of the rare earth metal, while in the case of calcium the rare earth content may be as high as 97%.

Mr. R. Manocha : Vapour phase reduction of rare earth salts as suggested in the discussion may present rather considerable practical difficulties because in general they have pretty high volatilisation points.

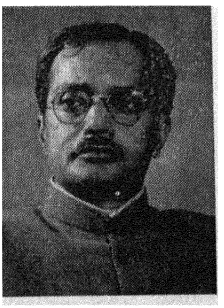
Author's reply : The boiling point of rare earth chlorides is not a criterion. If a high vapour pressure is obtained, it will be sufficient. It is difficult to find a material of construction such that it resists the attacks of rare earth chloride and magnesium vapours.

Contributors to the Proceeding

Dr. T. V. Arden, B.Sc., Ph.D., F.R.I.C., M.I.M.M., was born in Manchester, U.K. in 1918. He served with Royal Air Force as Navigator Leader, Madras Presidency Squadron 1941-45. At the end of the war, he was appointed Head of the Ore Concentration Section at the Chemical Research Laboratory, D.S.I.R. (Teddington, England), which position he occupied till 1952. Since 1952 he is serving as the Chief Metallurgist, The Permutit Co. Ltd., London. He is also Director, Ion Exchange (Canada) Ltd. In 1952 he was awarded Beilby Memorial Award administered by R.I.C., S. C. I. and Institute of Metals.



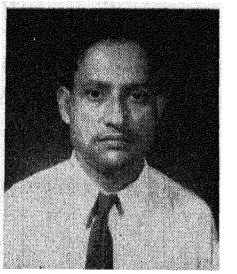
Mr. M. K. Asundi, Graduated in Met. Engg. from Banaras Hindu University and joined Indian Institute of Science for Research. Since 1955 he is working in Metallurgy Division of the Atomic Energy Establishment, Bombay.



Dr. T. Banerjee—was born in 1907 in East Bengal. He obtained his M.Sc. Degree from the Dacca University in 1930, and was awarded the D.Sc. Degree of the Dacca University for his work on "Photo-active properties of inorganic colloids". From 1945 to 1947 he carried out research at King's College, London and was awarded the Ph.D. Degree of the London University for his work on "Deposition of Alloys". He joined the National Metallurgical Laboratory, Jamshedpur, in 1948 and is now the Deputy Director of the Laboratory. He has been engaged on a variety of problems in Physical Chemistry, Electroplating and Chemical Metallurgy. He is the author of 93 papers and has 13 patents.

He is a Fellow of the Royal Institute of Chemistry (F.R.I.C.), The Institution of Metallurgists, London (F.I.M.), and also Fellow of the National Institute of Sciences, India. He is the Chairman of the Chemical Analysis Sectional Committee, SMDC 2 and the Electroplating Sectional Committee, ETDC 12 of the Indian Standards Institution.

Dr. R. Caillat—Born 12th November, 1921 is an Engineer of the Ecole Nationale Superieure de Chimie of Paris (1942) and Doctor of Physical Sciences Paris, (1945). He was a Research Attache to the National Centre of Scientific Research, Nuclear Chemistry Laboratory in 1945 and at present is Chief, Section of Solid State Chemistry of the Department of Metallurgy and Applied Chemistry.

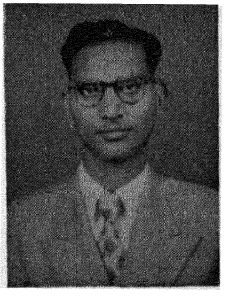


Mr. P. B. Chakravarti, is a Junior Scientific Officer of the Chemistry Division, National Metallurgical Laboratory, Jamshedpur. He graduated in 1936, with Honours in Chemistry from the University of Dacca and took his M.Sc., degree with a first class in 1938, with a research paper on Fischer-Tropsch synthesis. He has developed a combined chemical and electrochemical method which has been used successfully for preparation of beryllium oxide as well as oxides of Zirconium and titanium from zircon and ilmenite. He is author of 4 papers and a patent.

Dr. J. Friedel—Born in Paris in 1921. He went through the Ecole Polytechnique and the Ecole des Mines de Paris, and spent three years in Bristol (England) where he obtained a Ph.D. under Professor N. F. Mott. He is Docteur ès Sciences, Ingénieur en Chef du Corps des Mines, and now Maître de Conférence de Physique des Solides à la Faculté des Sciences de Paris.

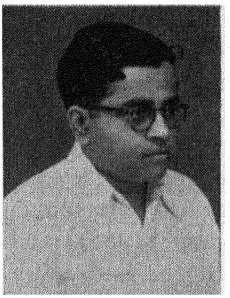
Dr. Henry H. Hausner—Born in Vienna, Austria. He received his education at the University of Vienna (E. E. and Dr. Eng.), then worked on design and construction of power plants, and became director of research in one of Austria's leading lamp factories. He came to the United States in 1940 and has served as Research Engineer for American Electro Metal Corporation, Chief Research Engineer for General Ceramics and Steatite Corporation, Research Associate and Adjunct Professor at New York University, and Manager of Atomic Energy Engineering at the Atomic Energy Division of Sylvania Electric Products Inc. In 1956 he became General Manager, then Vice President, of the Nuclear Engineering Division of Penn-Texas Corporation.

Dr. Hausner is Adjunct Professor of Metallurgy at the Polytechnic Institute of Brooklyn, and a member of numerous technical and scientific societies in many countries. In 1956 he received the Powder Metallurgy Achievement Award from Stevens Institute of Technology. Dr. Hausner is the author of more than 70 technical and scientific articles. He is the author of "Powder Metallurgy—Principles and Methods" (1947); co-author of Wulff's "Powder Metallurgy" (1943); co-author with Lustman and Kerze of "Metallurgy of Zirconium" (1955), with White and Burke of "The Metal Beryllium" (1955); and with Roboff of "Materials for Nuclear Reactors" (1955); and editor of "Powder Metallurgy in Nuclear Engineering" (1958).



Mr. S. K. Kantan (Born July 1929) is a graduate in Science of the Bombay University (1948) and B.Sc. (Tech.) in Chemical Engineering (1950). He was on the staff of the University Dept. of Chemical Technology during 1951—1953, and since April 1953, he is with metallurgy Division of the Atomic Energy Establishment.

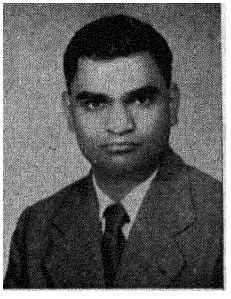
Mr. B. H. Krishna, B.Sc., Mysore University, 1926 ; M.Sc. (Bombay) 1929 was Research Scholar for the period 1926-29 in the Indian institute of Science, Bangalore. He is an Associate of Indian Institute of Science and of the Royal Institute of Chemistry of Great Britain ; and Member of the Institute of Chemical Egineers. He was appointed Industrial Probationer for training as Industrial Chemist and Chemical Engineer, Government of Mysore, in 1929 ; and served till 1943 as Chief Chemist and Chemical Engineer and as Adviser to the Government on chemical industrial developments; General Manager of Government Industrial & Testing Laboratory till 1943. He held the posts of General Manager, Sarabhai Chemicals, Baroda, 1943-48 ; Development Officer, Indian Penecillin Project, 1949-51; Head of the Division of Food Engineering, Central Food Technological Research Institute, Mysore, 1951-56 and is Chemical Engineer, Department of Atomic Energy, since 1956.



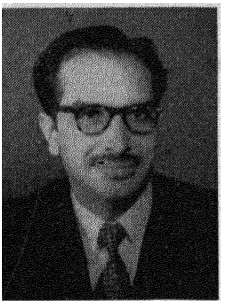
Dr. R. Krishnaswamy, passed his B.Sc. (Met.) from Banaras Hindu University in 1946 and M.S. and Ph.D. from Ohio State University in 1950 and 1951 respectively. He was Lecturer in the College of Mining and Metallurgy B.H.U. for the period 1946-47 and 1951-52. He was associated with the construction of the 'Chance' coal washing plant at Monongahela, Penna. Also worked at the Central Mill of the Eagle Picher Mining and Smelting Co. Ltd., and the Climax Molybdenum Co., U.S.A. He spent a few months at the Salt Lake City Experimental Station of the U. S. Bureau of Mines. Since 1953 he is Senior Scientific Officer, Ore dressing section of the Department of Atomic Energy.

Dr. Paul Krumholz—Born in Poland, August 30, 1909. Ph.D. (Vienna, 1933). Was Assistant to Prof. Feigl at the University of Vienna, 1930-1938. He became Scientific Director of Soc. Belge des Recherches et Etudes, Belgium, 1938-1940 and is Technical Director of Orquima S.A. Sao Paulo, Brazil, since 1942. He has worked in the field of analytical chemistry, the chemistry of coordination compounds and spectroscopy, on which he has a large number of publications. He has also worked on the technology of rarer metals, rare earths, thorium, uranium and indium etc.

Dr. S. Lawroski, graduated from The Pennsylvania State University in 1934 and received his Ph.D. in 1943. From 1934 to 1943 he was a research assistant at the Petroleum Refining Laboratory at State College, Pennsylvania. In 1043 he joined the Research Division of the Esso Laboratories of the Standard Oil Development Company (now Esso Research and Engineering Company), Flizabeth. New Jersey, as a research chemical engineer. From 1944 to 1946 he was loaned by the Standard Oil Development Company to the Manhattan Project's Metallurgical Laboratory at Chicago. In 1946 he rejoined the Standard Oil Development Company and was sent as one of its representatives to the Clinton Laboratories (now Oak Ridge National Laboratory) where he was an advanced professional trainee in the school for reactor engineering. In 1947 he joined the staff of the Argonne National Laboratory as Associate Director of the Chemistry Division. Since 1948, Dr. Lawroski has been Director of the Chemical Engineering Division. He has been engaged in separations process technology in atomic energy for more than 12 years. He has served as U.S. delegate to atomic energy conferences in Switzerland, France, United Kingdom and Belgium. Dr. Lawroski is a member of the Editorial Advisory Board for the Reactor Handbook published by the U.S.A.E.C. and is a member of the board of directors of the American Nuclear Society.

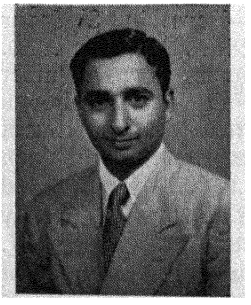


Dr. M. K. Madhekar—Born in Sholapur district, Bombay State; on 28th November 1930. Passed B.E. (Met) examination in December 1951 from the College of Engineering, Poona and worked in the heat treatment department of the Premier Automobiles Limited, Bombay, from Feb. 1952 to August 1953. He received his Ph.D. from Manchester University in July 1957 and worked in a steel foundry in W. Germany for a period of 4 months. At present working in the metallurgy division of the Atomic Energy Establishment, Government of India, as Junior Research Officer since March 1957.

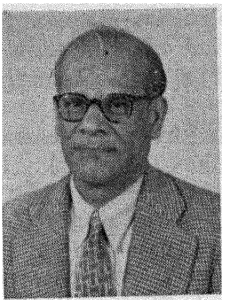


Mr. R. Manocha—Born at Ferozepore, Punjab in November, 1927 ; graduated with Honours in Chemistry from Delhi University in 1947, obtained D.I.I.Sc. (Metallurgy) from the Indian Institute of Science, Bangalore in 1950 and Dip. Perf. Met. (Diploma Advanced Course of Metallurgy), from Milan Polytechnic, Italy in 1955, against an award of Italian Govt. Scholarship. He is an Associate of the Institution of Metallurgists (A.I.M.) & Associate Member, Indian Institute of Metals. He has been engaged for the last 9 years in research connected with chlorination of minerals, measurement of cathodic overvoltages in fused electrolytes, Kroll's process for the preparation of titanium, zirconium-hafnium separation and regeneration of waste liquors from electrolytic manganese cells. While in Italy he toured various metallurgical industries and laboratories, connected with metal extraction and fabrication. He was with National Metallurgical Laboratory, Jamshedpur from 1951-56 and joined Extractive Metallurgy section of Metallurgy Division, Atomic Energy Establishment, Trombay, in 1956.

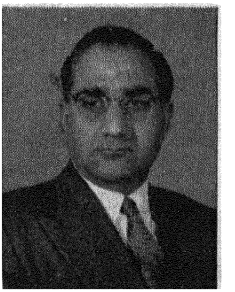
Mr. G. P. Mathur—Born in 1923, graduated in Metallurgy from the Banaras Hindu University in 1946. After a brief period with Messrs Cooper Engineering Ltd., Satara, joined the Ore Dressing Division of the National Metallurgical Laboratory in 1948. He has carried out research and development work on benefication of manganese and iron ores and on uranium bearing ores. He is the author of a number of papers and reports and is at present holding the post of Senior Scientific Officer.



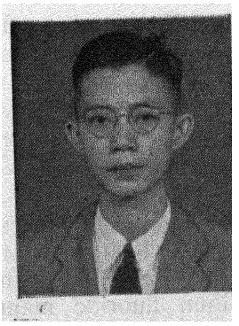
Dr. V. K. Moorthy—Born 10th March 1925 graduated from the Chemistry Department of the Andhra University, being awarded the B.Sc. (Hons.) degree in 1944 and M. Sc. in 1946. He was employed as a Research Assistant by the Council of Scientific and Industrial Research, during 1944-1948, he joined the Ceramics Department of the University of Illinois, where he obtained the M.S. (1950) and Ph.D. (1951) degrees. After his return from the States, Dr. Moorthy was with the Refractories Division of the National Metallurgical Laboratories during 1953-1956 and has been with the Metallurgy Division of the Atomic Energy Establishment since April 1956.



Mr. P. I. A. Narayanan—Graduated in Metallurgy in 1934 from Banaras. Worked as Assayer and Metallurgist in a tin-wolfram mine, Lower Burma 1935-38 ; as Mining Engineer and Metallurgist in the South India Gold Prospecting Co., Ltd , 1939-41 ; as a Metallurgist, Geological Survey of India 1942-45 ; as Mill Superintendent, Zawar lead-zinc mines of the Metal Corporation of India, 1946-47 and as Assistant Director, Ore Dressing Division, National Metallurgical Laboratory since 1948. He has visited important milling plants and ore testing laboratories in Australia on a U.N. Fellowship and has been awarded two silver medals and Government of India's cash prize for his research work. He is a Member of the American Institute of Mining and Metallurgical Engineers, Geological, Mining and Metallurgical Institute of India, Indian Institute of Metals and the Institute of Mining and Metallurgy, London.

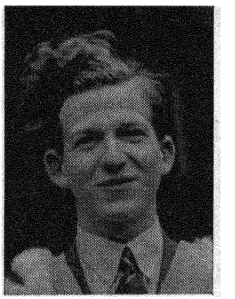


Dr. Balraj Nijhawan—Born September 22, 1915, was educated at Government College, Lahore and Banaras Hindu University. He took his Ph.D. (Sheffield) in 1941; and worked with the Tata Iron and Steel Co., Ltd., Jamshedpur, 1936-38, Research Officer, Government Metallurgical Inspectorate, Tatanagar, 1942-48. He joined the National Metallurgical Laboratory, 1948 as Assistant Director, became Deputy Director in 1953 and Director in 1957. One of his notable contributions is the development of stainless steel containing manganese and nitrogen, for which he was awarded the decoration PADMA SHRI in 1958. Dr. Nijhawan is author of more than 100 research papers and articles and is a member of various societies in the field of metallurgy in the United States, United Kingdom and in India.

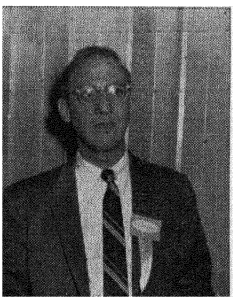


Mr. Kyaw Nyun—Immediately after graduating from the Rangoon University in 1949 joined the Metallurgy Research and Planning Section of the State Industrial Research Institute & worked on extraction of antimony and benefication of ores of antimony, lead and zinc. He is at present Senior Research Officer in the Metallurgy and Geology Research Department of the Union of Burma Applied Research Institute.

Dr. Brahm Prakash—Born on August 21, 1912, at Lahore and received his education at the Punjab University and at the Massachusettes Institute of Technology, Cambridge, Mass., U.S.A. He got his Ph.D. in Physical Chemistry in 1942 and Sc.D. in Metallurgy in 1948. He was with the Indian Railways as an Asstt. Metallurgist from 1940-45 ; with the Atomic Energy Commission as Metallurgist from 1948-50, and from 1951-57 Professor and Head of the Department of Metallurgy, at the Indian Institute of Science, Bangalore. He is at present Deputy Chief Scientific Officer (Metallurgy) in the Atomic Energy Establishment, Trombay. He is the author of several publications in physical chemistry and metallurgy, chiefly extractive metallurgy.



Mr. D. M. Poole, B.Sc., M.Sc., D.Phil.—Aged 28. Education at King's School, Macclesfield and Manchester University obtaining 1st class Honours in metallurgy in 1950. He was awarded an M.Sc. in 1951 for research on aluminium-magnesium alloys at Manchester and a D. Phil. at Oxford University for constitutional studies under Dr. W. Hume-Rothery. He joined the Atomic Energy Research Establishment in 1954 and is at present a Senior Scientific Officer working with plutonium alloys.

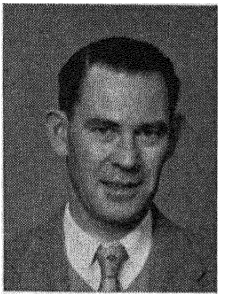


Mr. C. J. Schwenzfeier, Jr.—Obtained his Bachelor Degree in Metallurgy from Massachusetts Institute of Technology in January, 1941. After working at the Weatherhead Company, Cleveland, Ohio, he joined Brush Beryllium Company as process engineer early in 1941, was made head of the Engineering Department in 1943, Technical Manager in 1945, and in 1952, was elected Vice President, Engineering. He developed in 1944 the ammonium beryllium fluoride purification process for production of large quantities of nuclear grade beryllium metal. He also developed liquid extraction technique and chelation purification process for production of high purity beryllium hydroxide.

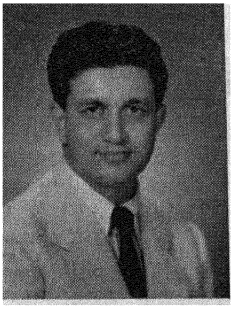
He developed, in 1952 the continuous beryllium hydroxide process, based on chelation of impurities and precipitation of Alpha beryllium hydroxide, and in 1948, in cooperation with Mr. Leland Conant, developed and engineered the continuous beryllium fluoride manu-

facturing process. In 1953, he engineered and constructed the world's largest powder metallurgy manufacturing equipment for the Brush Beryllium Company at Luckey, Ohio. This equipment produces full density beryllium powder metallurgy billets over five feet in diameter, two feet thick, and weighing up to 3,000 pounds.

Dr. Jagadish Shankar—Born in 1912 passed his B.Sc. in 1932; M.Sc. in 1934; Ph.D. in 1940; M.S. in 1948; He taught chemistry at the Royal Institute of Science, Bombay, St. John's College, Agra, Maharaja's College, Jaipur and the Delhi University as lecturer and Reader, from 1934-1949. He studied at Columbia University, New York 1946-48 and worked for sometime in 1948 in the Radioactivity Division of the National Bureau of Standards, Washington D. C. Joining the Atomic Energy Commission as Chemist in 1949, he is now head of the Chemistry Division, Atomic Energy Establishment, Trombay.

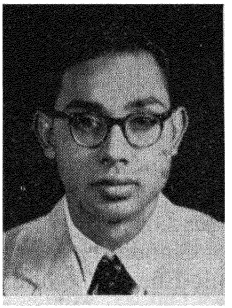


Dr. Thomas Robert Scott—Born in Melbourne, September 20, 1913. He was educated at Melbourne University, (B.Sc. 1934; M.Sc. 1936; B. Ed. 1938; D.Sc. 1949). He won the Howitt and Kernot Research Fellowship in Geology and the Grimwade Prize for Chemical Research in 1948; He was elected a Fellow of Royal Australian Chemical Institute in 1951. Holding the posts of Explosives Chemist for 1940-42 and Research Chemist at C.S.I.R.O. since 1942 he is at present Principal Research Officer in charge of uranium investigations at the Division of Industrial Chemistry, C.S.I.R.O. He is author of numerous publications and technical reports dealing with uranium investigations on Australian ores etc. and is interested in music, literature, gardening and squash.

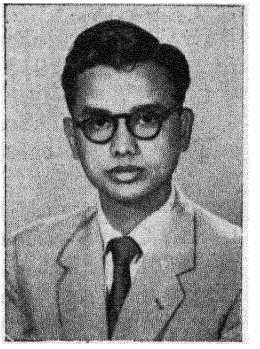


Mr. Homi Sethna—Born August 24, 1923 at Bombay, was educated at St. Xavier's School, St. Xavier's College and the Department of Chemical Technology of the Bombay University and at the Michigan University, U.S.A. B.Sc. (1941); B.Sc. (Tech.) (1944); M.SE. (1947). He worked in the dye-stuff division of the Imperial Chemical Industries at the Blackley Works, Manchester 1947-1948 and took training in Societe de Produits Chimiques des Terres Rares, France, 1949-1950. He is at present Works Manager, Indian Rare Earths (Private) Ltd., and looking after the Thorium Plant,

Trombay, and is also the Project Manager (India), Canada-India Reactor of the Atomic Energy Establishment. Mr. Sethna was associated with the construction and erection of the Rare Earths Factory at Alwaye and was responsible for the construction of the Thorium Plant and the Uranium Metal Plant at Trombay. He has been awarded the **Padma Shri** in 1959.



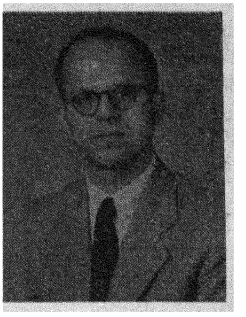
Mr. R. Somasundaram, after graduation from Madras University in 1953, joined Indian Institute of Science, Bangalore, obtained the diploma in metallurgy in 1955 and continued as a research scholar for about a year. He joined the Atomic Energy Establishment, Trombay, in 1956.



Mr. C. V. Sundaram—Born on November 7, 1929, at Ottappalam, Kerala and received his University education at the Presidency College, Madras. He took Honours Degree in Chemistry with distinction in 1949 and Diploma in Metallurgy of the Indian Institute of Science, Bangalore, in 1952. He joined the Metallurgy Division of the Atomic Energy Establishment (Trombay) as Junior Research Officer, in 1956 and has been working on the extraction and refining of zirconium for reactor applications.

Dr. K. Tangri—Born in Lahore, Punjab, on 15th March 1925, received B.Sc. Degree from Punjab University in 1944; B.Sc. (Met.) from Banaras Hindu University in 1948; M.S. (Met.) in 1952 and Ph.D. in 1954 from Missouri University (U.S.A.), He was formerly Production Metallurgist with Indian Smelting and Refining Co., Bombay; International Nickel Research Fellow and Argonne National Laboratory Research Fellow at Missouri University (U.S.A.), Research Associate in Metallurgy at Pennsylvania State University (U.S.A.), Guest Research Worker at National Bureau of Standards (Washington) U.S.A., and Guest Research Associate at Berg Akademie (West Germany). In 1956 he made a study tour,

visiting Universities and Research Establishments in U.K., in various countries on the continent and in U.S.S.R. At present he is attached to the Metallurgy Division of the Atomic Energy Establishment, Trombay, Bombay.



Dr. G. S. Tendolkar, after graduating in chemical engineering from the University of Bombay in 1942, he took his Ph.D. degree in Metallurgy from the University of Sheffield in 1947. After serving as a lecturer in the University Department of Chemical Technology and Victoria Jubilee Technical Institute, Bombay, he joined the Atomic Energy Establishment Trombay, Bombay, in 1953. He has devoted considerable attention to the metallurgy of uranium and thorium and is at present Principal Research Officer in charge of Beryllium Project.

Professor F. Trombe, Doctor of Sciences, Chemical Engineer, is Director of Research at the National Centre of Scientific Research, Director of Rare Earths Laboratory, C.N.R.S., Paris, and Director of Montlouis Solar Energy Laboratory, Eastern Pyreness. He has published valuable work on the separation of rare earths by different methods and has isolated in pure form gadolinium, dysprosium and europium. He has made valuable contributions on the subject of ferromagnetic properties of gadolinium and of dysprosium and curopium, and their allotropic modifications. He has constructed the world renowned solar furnaces of 2.5 KW, 60 KW and 1000KW with the help of which he has carried out researches on high temperature refractories etc.

Dr. D. N. Wadia, M.A., D.Sc., F.R.S., F.G.S., F.N.I. Born at Surat, October 25, 1883. He was educated at J. J. School, Surat and the Baroda High School and Baroda College He was Professor of Geology, Prince of Wales College, Jammu, Kashmir from 1907-1920 and with the Geological Survey, Government of India, from 1921-1938. He was Mineral Adviser, Ceylon Government from 1938-44 and from 1945-49, Mineral Adviser and First Director, Indian Bureau of Mines, Government of India. Since 1949, he is Geological Adviser, Atomic Energy Commission, Government of India.

Dr. Wadia is author of eighty-five Papers & Memoirs. In 1919 published the "Geology of India" now in its fifth edition. He is the Recipient of Medal of the Royal Geographical Society, London, 1934,

Lyell Medal of the Geological Society, London, 1943, Joyakishan Medal, Indian Society for the Advancement of Science, Calcutta, 1944, Jagdish Bose memorial Medal, Royal Asiatic Society, Calcutta, 1947, and Nehru medal, National Geographic Society, Banaras, 1950. He has been the President, Indian Science Congress, 1942 and 1943, National Institute of Science of India, 1945 and 1946, Geological Society of India, Calcutta University, 1937-38, Geological & Mining Institute of India, Calcutta, 1950, Central Board of Geophysics, Government of India, Delhi 1954-57, Geographers' Association of India, Delhi, 1955. He has represented India at international conferences, held in Australia, Europe and U.S.A.

Mr. M. B. Waldron, B.Sc. (Eng.), Ph.D., A.I.M. was born in London in 1924 and educated at Whitgift School, Croydon, studied Engineering in Kings College, London University from 1941 to 1943. He worked as a Junior Scientific Officer on aluminium alloy research at the Royal Aircraft Establishment, Farnborough until 1946. DSIR research assistant under Professor G. V. Raynor at Birmingham University from 1946-1948 and was awarded Ph.D. for constitutional studies on ternary and quaternary aluminium alloy systems. Since 1948, was employed in the Metallurgy Division of the Atomic Energy Research Establishment, Harwell on alloy development. where he is now a Principal Scientific Officer as Section Leader on plutonium metallurgy and reactor alloy developments.

Mr. L. M. Wyatt—Joined Atomic Energy Project in 1947 at AERE Harwell. He was responsible for development of fabrication processes for reactor core materials and investigations into effects of irradiation and was Incharge of metallurgical design of fuel elements for Calder Hall Reactor. He Joined Industrial group 2 years ago to take charge of Risley metallurgy section.